

Synthesis and Antioxidant Characteristics of Borate Esters Used in Lubricating Oil

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In the present studies, the preparation of esters of boric acid with hindered phenols is reported, wherein the alkyl groups are branched on the α -carbon atoms. The products were evaluated in terms of their oxidative stability. In most cases, improvements in oxidative stability in a hydrocarbon media (cumene) were observed.

Key Words: Borate esters, Hindered phenol, Lubricant additive, Antioxidant, Extreme pressure.

INTRODUCTION

Modern lubricants are formulated from a range of base fluids and chemical additives. The base fluid has several functions but primarily it is the lubricant, which provides a fluid layer separating moving surfaces or removing heat and wear particles while keeping friction at a minimum. Many properties of lubricants are enhanced or imparted by the addition of additives to the base fluid. For example, stability against oxidation and degradation in characteristic engine oil can be improved by the addition of antioxidants while extreme pressure antiwear properties needed in gear lubrication are created by the addition of special extreme pressure additives. The base fluid also functions as the carrier for these additives and must therefore be able to keep the additives in solution under all normal working conditions¹.

In recent years, much efforts have been focused on the research and development of new types of additives for lubricating oils without any environmental side effects². The trend in lubricant technology and specifically in passenger car motor oils, is to reduce the levels of phosphorus in the oil that comes from the antiwear additive called zinc dialkyl dithiophosphate (ZDDP). The current levels of phosphorus in motor oils is set at 0.10 % P and a movement is underway to reduce this to either 0.08 or 0.05 % P, with the eventual elimination of phosphorus altogether. The problem is maintaining adequate antiwear protection in the oil at a reasonable cost. The concern with P in motor oil is its poisoning effect on catalytic converters. Likewise, there is a movement toward reducing the overall presence of sulfur in motor oils, both because of environmental concerns, as well as because of the effect

of sulfur as a corrosive. As sulfur based compounds are now commonly used as anti-wear additives, there is a strong desire to reduce the amount of these compounds needed to achieve effective antiwear protection². Antioxidants used in lubricants include sulfides, disulfides, sulfoxides, phosphates, amines and phenols. Antioxidants produce SO_x and NO_x gases and phosphorous oxides¹. They poison the exhaust catalysts too.

It is commonly accepted that boron-containing compounds, *e.g.*, borate esters, not only have excellent antiwear and antifriction characteristics, but also possess good oxidation stability and compatibility with seals. Furthermore, they are non-volatile, relatively non-toxic and have a pleasant odor²⁻⁵.

However, a serious drawback which has restricted the use of borate esters is their susceptibility to hydrolysis in the presence of water. Some methods for improving the hydrolytic stability of borate esters are mentioned in the following items: (i) A hindered phenol inhibits hydrolytic attack on the boron-oxygen bonds⁶. (ii) The hydrolytic stability is improved by the addition of amine compounds which have non-bonding pairs of electrons. These amines coordinate with the electron deficient boron atom, preventing hydrolysis⁷. (iii) The hydrolytic degradation of borates is inhibited by the incorporation of certain diols in the lubricant formulation⁸. In this article, we wish to report the synthesis of some oil soluble borate esters and their antioxidant characteristics are investigated.

EXPERIMENTAL

All reagents and solvents were purchased from Merck Chemical Company and used without further purification. All yields refer to products isolated by column chromatography. IR spectra were run on a Perkin-Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity of both starting materials as well as the reaction products were checked by TLC on silica-gel polygram SILG/UV₂₅₄ plates or by a Shimadzu Gas Chromatograph GC-10A instrument with a flame-ionization detector using a 15 % carbowax 20 M chromosorb-w acid washed 60-80 mesh column.

Typical procedure for preparation of dihexyl (2,6-di-*t*-butylphenyl)borate (entry 2): In a round bottom flask, equipped with a Dean-Stark trap, 38.55 g of 1-hexanol (0.378 mol), 7.79 g of boric acid (0.126 mol) and 100 mL of toluene were heated to reflux the mixture. After azeotropically removing 6.8 mL of water the reaction in the Dean-Stark trap was believed to have completed since this was the expected amount of separating water in the reaction. Then, 26.00 g of 2,6-di-*t*-butylphenol (0.126 mol) was added to the mixture and distillation apparatus was then connected to the flask. Upon continuation of heating toluene and 1-hexanol were distilled off from the reaction mixture. The reaction was believed to be complete when no more 1-hexanol could be distilled from the mixture. The recovered product was a clear yellow liquid in 98 % yield.

MS: 150 (base peak), 205, 418.48 (M^+). 1H NMR ($CDCl_3$) δ : 6.7-7.2 (m, 3H), 3.7-4.0 (m, 6H), 1.2-1.6 (m, 29H), 0.9-1.0 (m, 9H) ppm. FT-IR (film, ν_{max} , cm^{-1}): 3056, 2983, 1715, 1455, 1375, 1266, 1107, 739.

The other compounds were prepared in a similar method. Their experimental results are summarized in Table-1. The spectroscopic data for these compounds are also shown below:

Trihexylborate B(C₆H₁₃O)₃: FT- IR (neat, ν_{max} , cm^{-1}): 2929, 2861, 1484, 1468, 1334, 1264, 1137, 1061, 927. 1H NMR($CDCl_3$), δ : 3.7-3.9 (t, $J = 9$ Hz, 2H), 1.3-1.7 (m, 8H), 0.8-1.0 (t, $J = 4.5$ Hz, 3H) ppm. Anal. calcd. (%): B 3.44, C 68.83, H 12.28. Found (%): B 3.2, C 70.0, H 12.4.

Hexyl-bis[2,6-di-*t*-butylphenyl]borate (entry 3): 1H NMR ($CDCl_3$) δ : 6.9-7.3 (m, 4H), 6.5-6.7 (m, 2H), 4.7-4.8 (m, 2H), 3.9-4.1 (m, 4H), 1.2-1.6 (m, 40H), 0.8-0.9 (m, 3H) ppm.

Tris[2,6-di-*t*-butylphenyl]borate (entry 4): 1H NMR ($CDCl_3$), δ : 6.7-7.2 (m, 3H), 1.1-1.4 (s, 18H) ppm.

Dihexyl[2,6-di-*t*-butyl-*p*-cresyl]borate (entry 5): 1H NMR ($CDCl_3$), δ : 6.7-7.2 (m, 2H), 3.7-3.9 (m, 8H), 2.2-2.4 (s, 3H), 1.2-1.6 (m, 27H), 0.9-1.0 (m, 9H) ppm. Mass: 150 (base peak), 205, 432.45 (M^+).

Hexyl-bis[2,6-di-*t*-butyl-*p*-cresyl]borate (entry 6): 1H NMR ($CDCl_3$) δ : 6.8-7.3 (m, 4H), 3.7-3.9 (m, 4H), 2.2-2.4 (s, 6H), 1.2-1.5 (m, 42H), 0.9-1.0 (m, 3H) ppm.

Tris[2,6-di-*t*-butyl-*p*-cresyl]borate (entry 7): FT- IR (neat, ν_{max} , cm^{-1}): 3530, 3226, 3030, 2997, 2921, 1509, 1496, 1408, 813. 1H NMR ($CDCl_3$) δ : 6.7-7.2 (m, 1H), 6.4-6.6 (m, 1H), 2.2-2.3 (s, 3H), 1.2-1.4 (s, 18H) ppm.

Triphenylborate (entry 8): 1H NMR ($CDCl_3$) δ : 6.8-7.0 (s, 5H) ppm. Mass: 76, 94 (base peak), 211, 290.15 (M^+).

Tris(*p*-cresyl)borate (entry 9): 1H NMR ($CDCl_3$) δ : 6.8-7.0 (s, 4H) 2.2-2.3 (s, 3H) ppm. Mass: 94 (base peak), 107, 332.23 (M^+).

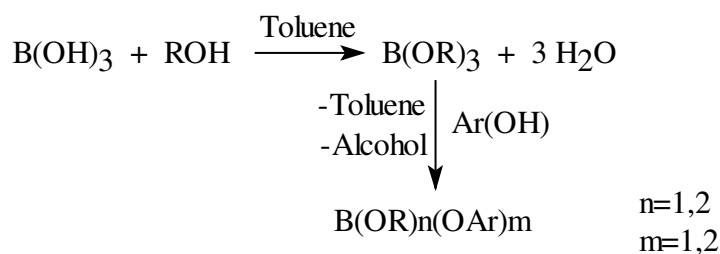
Oxidation test: The oxidation tests were carried out according to the reports⁹ as follow, in a jacketed reactor a 0.001 M solution of sample (containing additive and cumene) was placed while the temperature was set to 60 °C by circulating warm water through the reactor jacket. Then 0.2 g of azabisbutyronitrile was added and the oxygen pressure was set to 1 atm. The reduction in oxygen pressure was measured by a barometer.

RESULTS AND DISCUSSION

In this work, borate esters with a hindered phenolic group are synthesized. At first trialkyl borate such as tri-butyl, trihexyl and tris-(2-ethylhexyl)borate were prepared by reacting 3 mol of alcohol (1-butanol, 1-hexanol, 2-ethylhexanol, 1-nonanol) and one mole of boric acid in toluene. The produced water was separated in a Dean-Stark trap. Meanwhile, butanol and hexanol were reacted completely but 2-ethyl hexanol and nonanol resulted in 85 and 75 % yields, respectively.

The phenolic compounds such as phenol, *p*-cresol, 2,6-di-*t*-butylphenol and 2,6-di-*t*-butyl-*p*-cresol were added to the reaction mixture of trialkylborate prepared above (**Scheme-I**). The solvent and alcohol were distilled off. Mole ratios of phenolic compounds in the resulted alkylborate were determined on basis of the desired products (*e.g.*, mono, di or tri-substituent of phenolic compounds). When no further alcohol could be distilled off from the mixture, the reaction was believed to be complete. The products are also shown in Table-1.

In most environments in which lubricating oil is employed, it comes in contact with air, often at high temperatures and in the presence of metals or chemical compounds which act as "pro-oxidants" or oxidation catalysts. Under such conditions, the lubricant, whether it is a mineral or a synthetic ester based oil undergoes a complex series of oxidation reactions. The harmful results of such oxidation include principally an increase in the viscosity of the lubricant, the development of acidic contaminants such as "petroleum oxyacids" and the formation of carbonaceous matter. There is general agreement among independent investigators that the oxidation of lubricating oil involves a chain reaction in which initially formed organic peroxides attack unoxidized oil and is subsequently regenerated by oxygen in the air to continue such attack. According to this "peroxide theory", an effective anti-oxidant is a material which reduces organic peroxides and thereby causes the chain oxidation reaction to cease¹.



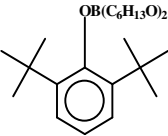
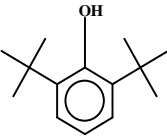
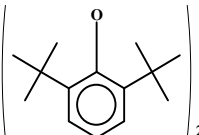
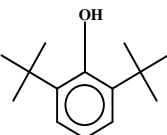
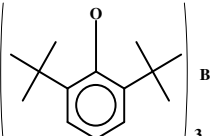
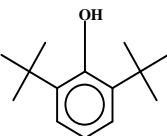
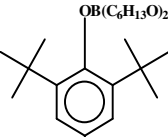
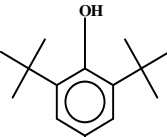
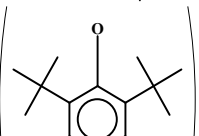
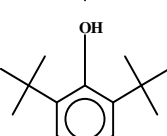
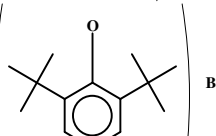
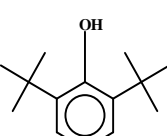
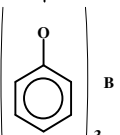
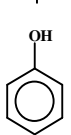
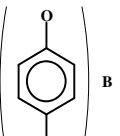
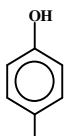
ROH = 1-Butanol, 1-hexanol;
ArOH = Phenol, *p*-cresol, 2,6-di-*t*-butylphenyl, 2,6-di-*t*-butyl-*p*-cresol

Scheme-I

The possibility that borate esters might act as chain breaking agents, by reaction with peroxy radicals, has been investigated in this work. A test method was used involving measurement of the oxidation rate of a suitable hydrocarbon containing an initiator such as azonitrile. Cumene oxidation in the presence of azonitrile was chosen as a suitable system^{12,13}. The oxidation reaction is readily initiated at 60 °C in the presence of oxygen.

The effects of borate esters and hindered phenols are shown in Figs. 1 and 2. These results clearly show that the borate esters can act as chain-breaking inhibitors.

TABLE-1
 REACTIONS OF BORIC ACIDS WITH ALCOHOLS AND PHENOLIC COMPOUNDS

Entry	Suggested structure	Phenol	Moles of phenol	Moles of alcohol	Moles of boric acid	Yield (%)
1	$B(OC_6H_{13})_3$	—	—	0.378	0.126	98
2			0.126	0.378	0.126	98
3	 BOC_6H_{13}		0.252	0.378	0.126	95
4	 B		0.378	0.378	0.126	97
5			0.126	0.378	0.126	95
6	 BOC_6H_{13}		0.252	0.378	0.126	96
7	 B		0.378	0.378	0.126	95
8	 B		0.378	0.378	0.126	95
9	 B		0.378	0.378	0.126	96

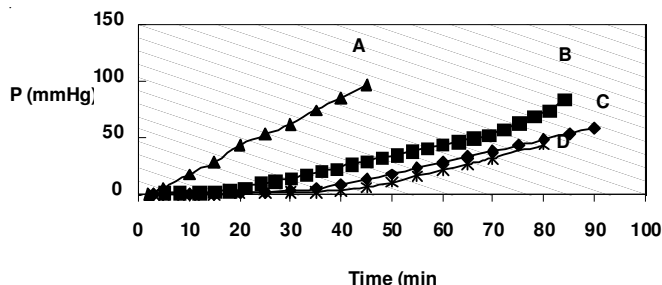


Fig. 1. Effect of phenolic compounds (0.001 M) on the oxidation of cumene A: No oxidant (0 min), B: 2,6-di-*t*-butyl-*p*-cresol (20 min), C: 2,6-di-*t*-butylphenol (35 min), D: phenol (40 min)

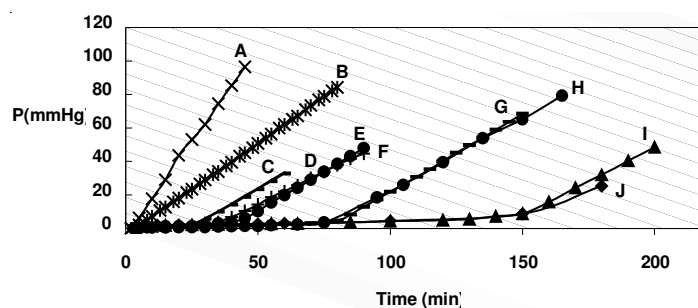


Fig. 2. Effect of borate ester (0.001 M) compounds on the oxidation of cumene A: No oxidant (0 min), B: trihexylborate (0 min), C: dihexyl[2,6-di-*t*-butylphenyl]borate (35 min), D: dihexyl[2,6-di-*t*-butyl-*p*-cresyl]borate (35 min), E: triphenylborate (40 min), F: tris(*p*-cresyl)borate (40 min), G: hexyl-*bis*[2,6-di-*t*-butylphenyl]borate (75 min), H: hexyl-*bis*[2,6-di-*t*-butyl-*p*-cresyl]borate (75 min), I: tris[2,6-di-*t*-butylphenyl]borate (150 min), J: tris[2,6-di-*t*-butyl-*p*-cresyl]borate (150 min)

As it could be inferred from these figures that the borates with tri substituted phenolic compounds inhibit oxidation reaction for a longer period of time. That inhibition occurs from the beginning of oxidation under mild temperature conditions, indicating that borate esters remove peroxy radicals. In another experiment, commercial antioxidant zinc dialkyldithiophosphate was used and the inhibition time of oxidation reaction found to be for 20 min though this result was 150 min for tris[2,6-di-*t*-butyl-*p*-cresyl]borate.

Conclusion

In conclusion, this method could be useful for preparation of oil soluble borate esters. These compounds are excellent antioxidants for hydrocarbons and lubricants (such as engine oil) in comparison with commercial antioxidants (zinc dialkyldithiophosphate). The borate esters are environmentally friendly additives. They do not contain heavy metals, do not poison exhaust catalysts and decompose in environment.

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REFERENCES

1. R.M. Mortier and S.T. Oraszulik, Chemistry and Technology of Lubricants, Edmundsbury Press, 1997. L.R. Rudnick, Lubricant Additives: Chemistry and Application, M. Dekker, edn. 2, New York, (2003).
2. J.B. Yao, Q.L. Wang, S.Q. Chen, J.Z. Sun and J.X. Dong, *Lubrication Sci.*, **14**, 416 (2002); C. Boshui, F. Jianhua, W. Jiu, L. Jia and L. Fang, *J. Rare Earths*, **26**, 590 (2008).
3. M. Braid, US patent US 4530770 (1985). M. Braid, US patent US 4474670 (1984).
4. J.B. Hinkamp, US patent US 3356707 (1967).
5. M.C. Croudace, US patent US 4701274 (1987).
6. M. Braid, US patent US 4547302 (1985).
7. V.R. Small and T.V. Liston, US patent US 4975211 (1990); J. Yao and J. Dong, *Lubrication Eng.*, **51**, 475 (1995).
8. E.W. William and T.D. Bryan, US patent US 4892670 (1990).
9. A.J. Burn, *Tetrahedron*, **22**, 2153 (1966).

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