Effect of Haloaryl Ethers on the Oxidative Stability of Polyphenyl Ethers

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Haloaryl ethers were effective oxidative stabilizers for polyphenyl ethers at 600° F. Although the degree of stabilization by the various additives varied, neither the type of halogen substituent nor its position within the ether structure was critical for effective stabilization. When present in low concentrations, the haloaryl ethers had no detrimental effect on the thermal stability of the polyphenyl ethers at 825° F.

SYNTHETIC lubricants have found increasing use as the severity of operating conditions for oil in aircraft, pumps, and space applications has increased. The polyphenyl ethers are a class of synthetic lubricants having outstanding oxidative and thermal stabilities. Moreover, their resistance to radiation enables them to be used in *gamma*-radiation environments (*7, 8*). The preparation and the physical and chemical properties of the polyphenyl ethers are discussed in detail by Mahoney and Barnum (*6*). Although the polyphenyl ethers are highly stable to heat and oxidation, an increase in their oxidative stability is desirable for economic reasons. Since the stability of these ethers is already high, conventional stabilizers are generally ineffective (*8*). Organotin compounds (*5*), cobalt salts (*1*), and phthalimide (*2*) have been described as oxidative stabilizers for polyphenyl ethers at high temperatures. This paper reports the use of haloaromatic ethers for this application.

EXPERIMENTAL

The polyphenyl ethers were prepared by a modified Ullmann procedure (*9*). With some modification, this procedure was extended to the preparation of the haloaryl ethers. Molecular distillation of the crude products was performed with a centrifugal molecular still (Consolidated Electrodynamics Corp.). An x-ray spectrometer (General Electric Co.) was used to determine the halogen content of the ethers. VPC analyses of the crude products indicated the presence of usually <10% volatile impurities. Yields of crude products were >85%. Since molecular distillation required leaving a substantial quantity of product in the residue, yields of distilled products are not reported.

Oxidative Stability Test. A modified Dornte apparatus was used for determining the oxidative stabilities of the polyphenyl ethers (*4*). A 10-gram sample of the ether was maintained in a glass cell at 600° F. in a closed system. Oxygen was passed through Ascarite and Drierite tubes, then bubbled through the sample at a rate of 50 ml. per minute by a small bellows pump. The immersed portion of the oxygen bubbler tube was wound with copper wire, which served as an oxidation catalyst. The system was maintained at constant pressure (atmospheric) by a mercury manostat which controlled a motor-driven, stainless steel bellows. The test was complete when 224 ml. of oxygen had been absorbed. The stability was expressed as the Dornte 0.5-mole time—that is, the time required for the absorption of 0.5 mole of oxygen by 500 grams of sample. *These tests should be conducted behind shields. During the course of several hundred runs, three explosions occurred in the vapor above the samples.*

Thermal Stability Test. A 5-gram sample of the ether was placed in a stainless steel tube equipped with a needle-valve vent and a rupture disc. The tube was then evacuated and purged 3 times with either nitrogen or helium. After the final evacuation to <1.0 mm., the tube was sealed and maintained at 825° F. for 48 hours. The thermal assay of the ether was made by gas chromatography and expressed as the percentage of sample that remained after it had been heated for 48 hours at 825° F.

Polyphenyl Ethers I and II. Mixtures of isomeric bis(phenoxyphenoxy)benzenes (I) and isomeric bis(phenoxyphenyl) ethers (II) were prepared by reaction of the appropriate mixture of isomeric dibromobenzenes or isomeric bromodiphenyl ethers with *m*-phenoxyphenol at 185° to 190° C. Mixtures of isomers were used to avoid crystallization during handling. Crude I and II were made practically halogen-free by heating with 5 wt. % KOH at 225° C. for 4 hours; the total halogen content was <0.005%.

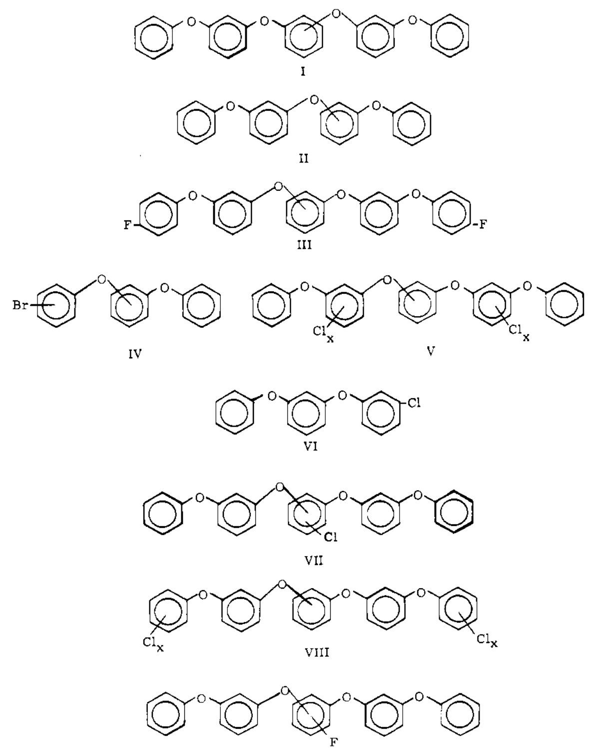

Figure 1. Structures of compounds I to IX.
In structures V and VIII, *x* = 0, 1, or 2

Mixture of Isomeric Bis[(*p*-fluorophenoxy)phenoxy]benzenes (III). A mixture of isomeric dibromobenzenes (85% *m*-, 10% *p*-, 5% *o*-) was treated at 185° to 190° C. with an excess of the potassium salt of *m*-(*p*-fluorophenoxy)phenol. The crude product was purified by molecular distillation to obtain III as a yellow, viscous oil containing 7.9% fluorine.

Mixture of Isomeric (Bromophenoxy)(phenoxy)benzenes (IV) and Polyphenyl Ether I. A mixture of isomeric dibromobenzenes was treated at 180° C. with an excess of the potassium salt of *m*-phenoxyphenol. The product was separated by molecular distillation into a colorless liquid mixture of polyphenyl ether I and isomeric bromoaryl ethers IV. This mixture contained 0.086% bromine.

Mixture of Isomeric Chloro-Substituted Bis(phenoxyphenoxy)-benzenes (V), Bromoaryl Ether IV, and Polyphenyl Ether I. Chlorine was bubbled into *m*-phenoxyphenol at 60° C., with stirring and cooling, until the weight of the reaction mixture had increased 3%. The resulting oily liquid was dissolved in benzene. The benzene solution was washed with 5% aqueous NaOH and then with water. The benzene was removed, and the residue was distilled under reduced pressure to obtain the chlorinated *m*-phenoxyphenol, a yellow oil (b.p. 140° C. at 1 mm.). Reaction of the potassium salt of this product at 180° C. with a mixture of isomeric dibromobenzenes gave a colorless, liquid mixture of isomeric haloaryl ethers IV and V, and some polyphenyl ether I. This mixture contained 1.2% chlorine and 2% bromine. Chloroaryl ether V was prepared primarily as the dichlorinated variety, although some monochlorinated product was also prepared.

Mixture of (*m*-Chlorophenoxy)(phenoxy)benzenes (VI) and Polyphenyl Ether I. *m*-Dichlorobenzene was treated in an autoclave at 220° C. with an excess of the potassium salt of *m*-phenoxyphenol. The product was separated by molecular distillation into a nearly colorless liquid mixture of chloroaryl ether VI and polyphenyl ether I containing 2.12% chlorine.

Mixture of Isomeric Bis(phenoxyphenoxy)chlorobenzenes (VII). A mixture of isomeric dibromochlorobenzenes was treated at 180° C. with an excess of the potassium salt of *m*-phenoxyphenol. The crude product was purified by molecular distillation to obtain VII, a pale yellow oil which contained 5.46% chlorine.

Mixture of Isomeric Chloro-Substituted Bis(phenoxyphenoxy)-benzenes (VIII) and Polyphenyl Ether I. Chlorine was bubbled into polyphenyl ether I at 50° to 60° C. until the weight of the reaction mixture had increased 5%. The oily liquid was dissolved in benzene. The benzene solution was washed with 5% aqueous NaOH and then with water. The benzene was removed, and the crude product was purified by molecular distillation to obtain a colorless liquid mixture of isomeric chloroaryl ethers VIII and polyphenyl ether I. This mixture contained 3.93% chlorine. Chloroaryl ether VIII was prepared primarily as the monochlorinated variety, although some dichlorinated product was also prepared.

Mixture of Isomeric Bis(phenoxyphenoxy)fluorobenzenes (IX). A mixture of isomeric dibromofluorobenzenes was treated at 180° C. with an excess of the potassium salt of *m*-phenoxyphenol. The crude product was purified by molecular distillation to obtain IX, a yellow oil which contained 3.3% fluorine.

Blends of Polyphenyl Ethers I and II With Haloaryl Ethers III-IX. Mixtures prepared from polyphenyl ethers I and II and haloaryl ethers III-IX were blended by stirring for 30 minutes at 120° C. The total halogen content of the blends was usually ≦0.04%.

DISCUSSION

Haloaryl ethers III-IX, having the halogen substituents positioned either randomly among the various rings or on specific rings, were used to stabilize halogen-free, distilled samples of polyphenyl ethers I and II.

Table I shows the oxidative stability of the haloaryl ethers tested. The Dornte 0.5-mole times of the chloro and bromo derivatives were much higher than those of the unstabilized polyphenyl ethers, indicating clearly the stabilizing effect of the halogens. The fluoro derivatives failed to provide this stabilization at a high concentration (7.9%), possibly because material of low oxidative stability was present in the haloaryl ethers. Since iodo compounds undergo thermal cleavage and hydrolysis at high temperatures, these compounds were not investigated. Under the thermal test conditions, samples of ethers containing >1% halogen decomposed to form glassy products. As a result, data on the thermal stabilities of the haloaryl ethers are not reported.

Three vapor-phase explosions occurred during Dornte oxidation stability tests. All took place at atmospheric pressure a short time after oxygen flow through the samples was begun. A trace of the solvent used during separation of the ethers (heptane) was detected in the unoxidized material from which two of the test samples (undistilled) were obtained. The explosions probably were due to the heptane vapors. Traces of heptane were still present after stirring the polyphenyl ether samples at 200° C. for 4 hours at 1 mm.

The effect of halogen concentration on the oxidative and thermal stabilities of polyphenyl ether I is shown in Table II. The variation in the Dornte 0.5-mole times of different unstabilized samples was probably caused by undetected trace impurities of unknown composition; however, the Dornte 0.5-mole times and the thermal assays for the same sample were reproducible (±1 hour and ±1%, respectively). Although the degree of stabilization by the various additives varied, the data show that neither the type of halogen nor its position in the structure of the polyphenyl ether was critical for effective stabilization. The oxidative stability of I was increased with increasing halogen content when V was used as the stabilizer. The data also indicate that V was the most effective stabilizer for I. However, this is not certain, since unknown stabilizers may have been present in the mixtures of the isomeric haloaryl ethers. Halogen concentrations from 0.02 to 0.04% had an observable but insignificant lowering effect on the thermal stability of I.

Table III shows the effect of halogen concentration on oxidative and thermal stabilities of polyphenyl ether II. Samples of polyphenyl ether II had higher initial oxidative stabilities than samples of polyphenyl ether I (Dornte 0.5-mole times: 25 hours *vs.* 20 hours). However, II was less affected by the haloaryl ether stabilizers than I. A blend

Table I. Oxidative Stability of Haloaryl Ethers

Unstabilized Samples of Polyphenyl Ether I			Haloaryl Ethers			
	Analysis			Analysis		
Dornte 0.5-Mole Time, Hr.	Halogen	Content	Compound	Halogen	Content, %	Dornte 0.5-Mole Time, Hr.
16	Br	0.003	III	F	7.90	19
15		0.000	IV	Br	0.09	39
20		0.000	V[a]	Cl	1.20	>60
		0.000		Br	2.00	
20		0.000	VI	Cl	2.12	55
20		0.000	VII	Cl	5.46	. . .
20		0.000	VIII	Cl	3.93	>60
20		0.000	IX	F	3.30	. . .

[a] Mixture containing IV.

Table II. Effect of Halogen Concentration on Oxidative and Thermal Stabilities of Bis(phenoxyphenoxy)benzene (I)

Unstabilized Samples of Polyphenyl Ether I				Stabilized Samples of Polyphenyl Ether I				
Dornte 0.5-Mole Time, Hr.	Thermal Assay, %	Analysis		Blending Material	Analysis		Dornte 0.5-Mole Time, Hr.	Thermal Assay, %
		Halogen	Content, %		Halogen	Content, %		
16	96	Br	0.003	III	F	0.040	21	93
15	89		0.000	IV	Br	0.030	27	88
20	96		0.000	V^a	Cl	0.007	40	96
					Br	0.013	40	
20	96		0.000	V^a	Cl	0.022	56	93
					Br	0.041	56	
20	96		0.000	VI	Cl	0.030	24	94
20	96		0.000	VII	Cl	0.030	37	96
20	96		0.000	VIII	Cl	0.020	27	96
20	96		0.000	IX	F	0.030	25	96

[a] Mixture containing IV.

Table III. Effect of Halogen Concentration on Oxidative and Thermal Stabilities of Bis(phenoxyphenyl) Ether (II)

Unstabilized Samples of Polyphenyl Ether II			Stabilized Samples of Polyphenyl Ether II				
Dornte 0.5-Mole Time, Hr.	Thermal Assay, %	Halogen Content	Blending Material	Analysis		Dornte 0.5-Mole Time, Hr.	Thermal Assay, %
				Halogen	Content, %		
25	96	0.000	VIII	Cl	0.02	28	94
25	96	0.000	VIII	Cl	0.03	29	94

of II and VIII containing 0.02% chlorine had a Dornte 0.5-mole time of 28 hours (an increase of 3 hours over that of unstabilized II), whereas a blend of I and VIII containing 0.02% chlorine had a Dornte 0.5-mole time of 27 hours (an increase of 7 hours over that of unstabilized I). No differences were observed between the thermal stabilities of the stabilized and unstabilized samples of II under the test conditions used.

These data demonstrate the effectiveness of haloaryl ethers as oxidative stabilizers for the polyphenyl ethers. Although a wide variety of other haloaryl compounds was not investigated, the stabilization appears to be specific to the haloaryl ethers; for example, chlorinated and brominated terphenyls were ineffective as stabilizers.

Previous mechanistic studies (*3*) showed that the oxidative degradation of polyphenyl ethers is essentially a free radical process, probably involving a hydroperoxide as an initial oxidation product. Although these data do not permit mechanistic interpretations, haloaryl ethers either function as radical scavengers or react with nonradical, chain-propagating species, such as phenols or hydroperoxides, to stop the chain process.

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