

Energetics of Some Bromine-Containing Aromatic Fire Retardants from Luminescence Properties*

INTRODUCTION

The pervasive and promising use of bromine-containing compounds as fire retardants in selected fibers, films and plastics is well documented.^{1,2} Particularly in aromatic compounds, the substitution of one or more hydrogens by bromine increases the resistance to flammability of systems where the bromine-containing compounds may be either nonpolymeric additives or where they are an integral part of the polymer structure.

In an attempt to find some common property suitable for the screening of bromine-containing aromatic compounds as fire retardants, an investigation was made of the photophysical properties of an unrelated series of fire compounds which have been reported as fire retardant chemicals and monomers.

EXPERIMENTAL

Ultraviolet spectra of the compounds were obtained using a Cary model 118C spectrophotometer. Phosphorescence spectra were recorded from a Perkin-Elmer model MPF-3 fluorescence spectrophotometer using a low-temperature phosphorescence attachment. The phosphorescence mean lifetimes were measured using a Tektronix model 5103N storage oscilloscope.

Reagent grade *o*-xylene and heptane and Spectroquality methanol (Matheson, Coleman, and Bell) were used for the recrystallizations. Hexane (UV grades) (Burdick and Jackson) and USP 95% ethanol, purified by distillation^{3,4} were used in the absorption and luminescence measurements. The 4,4'-(1-methylethylidene)bis(2,6-dibromophenol)(tetrabromobisphenol-A), 2,2'-((1-methylethylidene)bis((2,6-dibromo)4,1-phenyleneoxy)bisethanol [the bis(hydroxyethyl ether) of tetrabromobisphenol-A], and 1,1'-oxybis(2,3,4,5,6-pentabromo benzene) (decabromodiphenyl ether) were obtained from the Dow Chemical Co. The 4,4'-sulfonylbis(2,6-dibromophenol)-(tetrabromobisphenol-S) and the dimethyl ester of 2,5-dibromo-1,4-benzenedicarboxylic acid (dimethyl 2,5-dibromoterephthalate) were obtained from Great Lakes Chemicals Co. and American Enka Co., respectively.

Purification of Compounds

The tetrabromobisphenol-A (TBBPA), tetrabromobisphenolS (TBBPS), bis(hydroxyethyl ether) of TBBPA (ETBBPA), and dimethyl 2,5-dibromoterephthalate (DBDMT) were purified by successive recrystallizations from Spectroquality methanol. The decabromodiphenyl ether (DBDPE) was purified by successive recrystallizations from an *o*-xylene/heptane mixture.

RESULTS AND DISCUSSION

Absorption

The absorption spectral data for TBBPA, TBBPS, ETBBPA, DBDMT, and DBDPE are in Table I. The TBBPA, TBBPS, ETBBPA, and DBDMT spectra were measured in 95% ethanol between 200 and 350 nm.

When the data in Table I are compared to the absorption data for the unbrominated analogs of the compounds (Table II), it can be seen that some of the bands of the unbrominated compounds have shifted to longer wavelengths in the brominated compounds. This is to be expected when the heavy atom effects are considered.⁵⁻⁸ Thus, the 292.7-nm band of TBBPA is believed to be the

* This note was extracted, in part, from a thesis submitted by T. E. Davidson to Clemson University in partial fulfillment of the requirements for the degree of Master of Science in Textile Chemistry, August 1979.

TABLE I
Absorption Characteristics of the Brominated Compounds in 95% Ethanol

Compound	λ (nm)	ϵ^a
Tetrabromobisphenol-A	205.8	42,220
	292.7	5,811
Tetrabromobisphenol-S	223.9	19,670
	313.2	25,660
Dimethyl 2,5-Dibromoterephthalate	215.2	46,670
	291.0	3,631
bis(Hydroxyethyl ether) of tetrabromobisphenol-A	207.8	48,300
	277.0	1,790
Decabromodiphenyl ether ^b	284.4	1,954
	227.6	47,780
	275.0	2,782
	305.8	1,453

^a Units are liter/cm/mole.

^b In hexane.

comparable band that appears at 275 nm in bisphenol-A. In the same way the 313.2-nm band of TBBPS corresponds to the 262-nm band of bisphenol-S, the 291-nm band of DBDMT is the 286.2-nm band in dimethyl terephthalate (DMT), and the 275.0-nm band of DBDPE corresponds to the 271-nm band of diphenyl ether (DPE).

TABLE II
Absorption and Phosphorescence Characteristics of the Unbrominated Analogs

Compound	Absorption spectra			Ref.
	λ (nm)	ϵ (liter/cm/mole)	Solvent	
Bisphenol-A	227.0	25,120	Ethanol	9
	275.0	6,309		
Bisphenol-S	236.0	13,180	Ethanol	10
	262.0	19,950		
	295.0	2,239		
Dimethyl terephthalate	241.2	20,630	Ethanol	4
	286.2	2,074		
	191.0	40,620	Hexafluoro-isopropanol	
Diphenyl ether	224.0	11,220	Ethanol	11
	271.0	2,042		
Compound	Phosphorescence spectra			Ref.
	E_x (nm)	E_m (nm)	τ (sec)	
Dimethyl terephthalate	252	391	2.2 ^a	4
		404		
		418		
		432		
Diphenyl ether	234	404	0.45	12
		264		

^a The value reported was 252 nm for E_x , and 418 nm for E_m .

TABLE III
Phosphorescence Characteristics of the Brominated Compounds

Compound	E_x (nm)	E_m (nm)	τ (sec) ^a	λ_s (nm) ^b	E (kcal/mole)
Tetrabromobisphenol-A	322	450	0.75	399.5	71.68
Tetrabromobisphenol-S	290	408		370	77.39
	290	430			
	325	408			
	325	430			
Dimethyl 2,5-dibromoterephthalate	328	445		397	72.13
<i>bis</i> (hydroxyethyl ether) of tetrabromobisphenol-A	255	444	1.00	367.5	77.92
	290	444	1.00		
	300	444	1.50		
Decabromodiphenyl ether	350	466		431.5	66.36
	350	495			

^a Where no τ value is given, the value was measured as being less than 0.2 sec, which is unreliable.

^b The wavelength at which the emission spectrum first leaves the baseline.

The new peak in DBDMT (215.2 nm) may be explained by comparing it to data obtained for DMT by Cheung⁴ who reported a peak at 191 nm ($\epsilon = 40,620$ liter/cm/mole) in hexafluoroisopropanol (HFIP). Thus, the 215.3-nm peak of DBDMT, which has an extinction coefficient of 46,670 liter/cm/mole, is probably the same band shifted because of the heavy atom effect. The 205.8-nm peak of TBBPA and the 223.9-nm peak of TBBPS may be explained in a similar fashion.

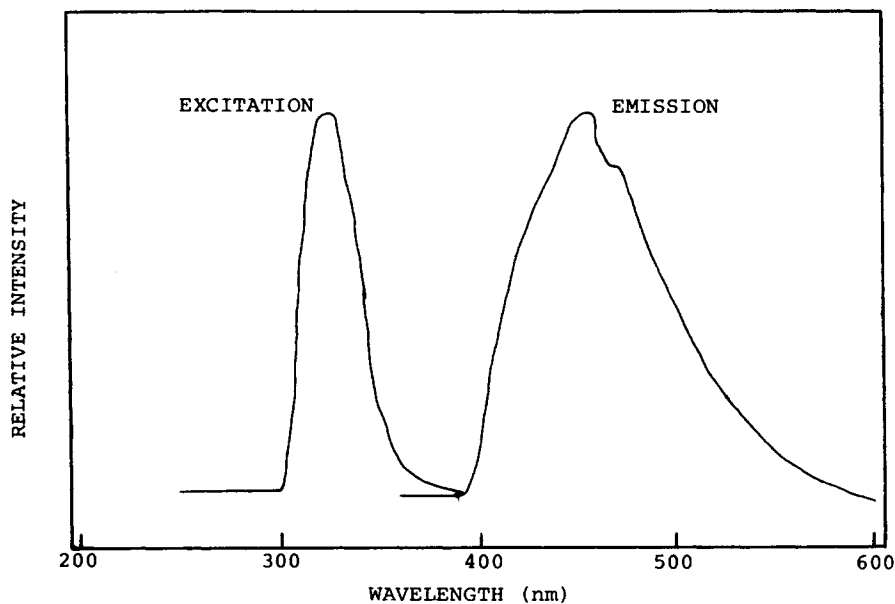


Fig. 1. Phosphorescence excitation and emission spectra of tetrabromobisphenol-A, at 77 K; excitation scan: $E_m \lambda 450$ nm; emission scan: $E_x \lambda 322$ nm.

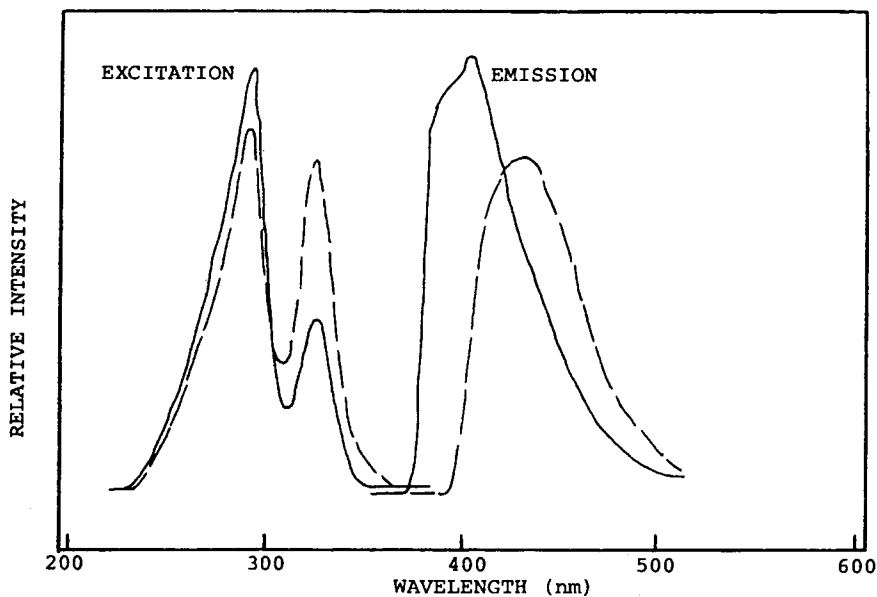


Fig. 2. Phosphorescence excitation and emission spectra of tetrabromobisphenol-S, at 77 K; excitation scan: $Em \lambda$ (—) 408 nm, (---) 430 nm; emission scan: $Ex \lambda$ (—) 290 nm, (---) 325 nm.

Luminescence

The phosphorescence excitation and emission spectral data for the brominated compounds are given in Table III and Figures 1–5. Phosphorescence data for the unbrominated analogs, DMT and DPE are given in Table II. Unlike their unbrominated analogs, DBDMT and DBDPE do not fluoresce.^{4,12} The ICS ($^3T_1 \leftarrow ^1S_1$) competes¹³ to cause the DBDMT and DBDPE to not fluoresce

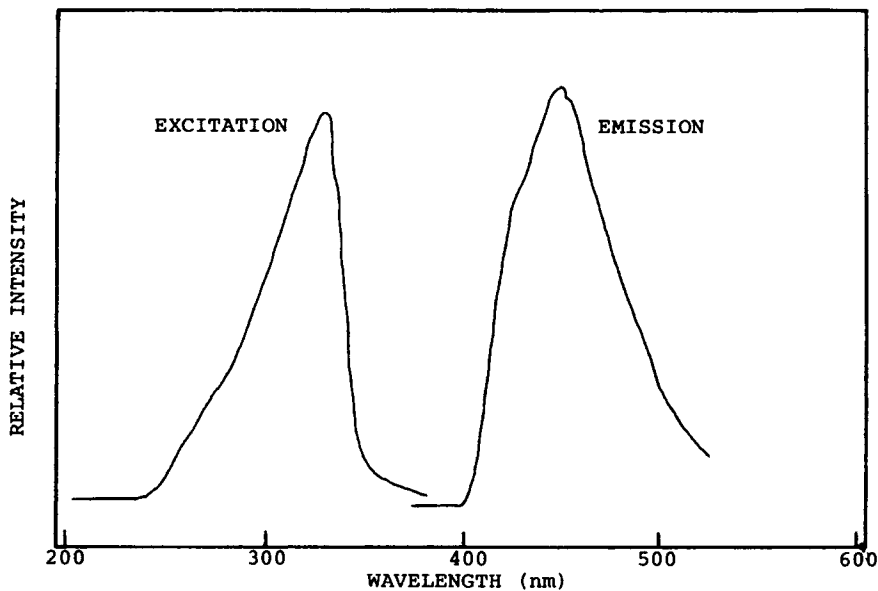


Fig. 3. Phosphorescence excitation and emission spectra of dimethyl 2,5-dibromoterephthalate, at 77 K; excitation scan: $Em \lambda$ 445 nm; emission scan: $Ex \lambda$ 328 nm.

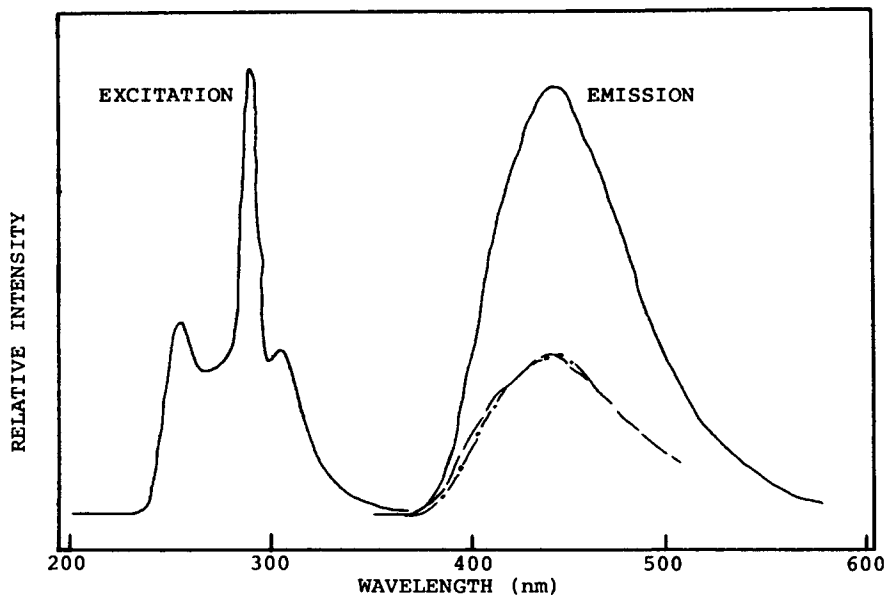


Fig. 4. Phosphorescence excitation and emission spectra of the *bis*(hydroxyethyl ether) of tetrabromobisphenol-A, at 77 K; excitation scan: $E_m \lambda$ 444 nm; emission scan: $Ex \lambda$ (—) 290 nm; (---) 255 nm, (- - -) 300 nm.

in contrast to their unbrominated analogs which do. It should be noted that while the DBDMT emission collapses to a single peak compared to that for DMT, the DBDPE, when compared to DPE, expands to a double maxima of the strongest emission in the unbrominated compounds, as shown by the shift from 418 nm for DMT to 445 nm for DBDMt and from 404 nm for DPE to 466 nm for DBDPE.

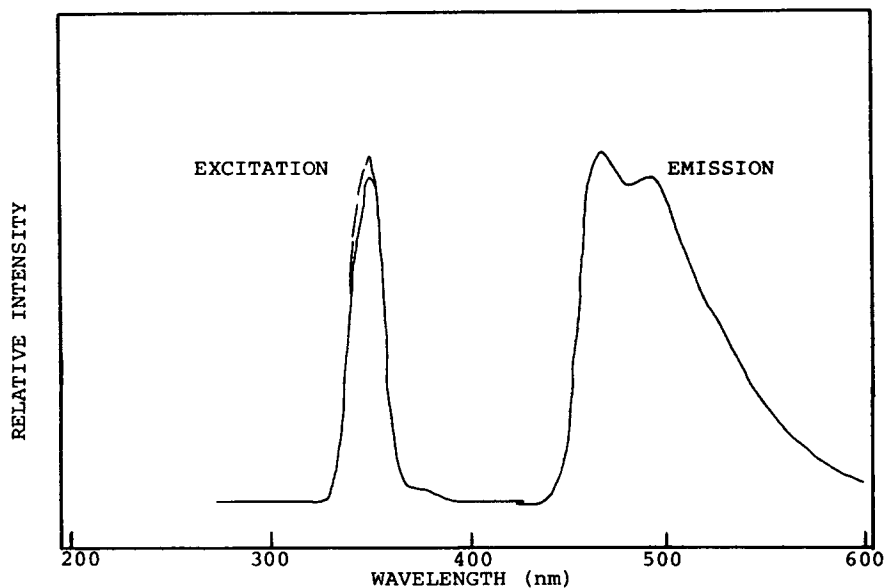


Fig. 5. Phosphorescence excitation and emission spectra of decabromodiphenyl ether, at 77 K; excitation scan: $E_m \lambda$ (—) 495 nm, (---) 466 nm; emission scan: $Ex \lambda$ 350 nm.

In many cases, the polymers containing these flame retardants are capable of undergoing thermal and photolytic degradation. If the polymers are to degrade photolytically, the responsible excited chromophore should contain enough energy to initiate the degradation. The emission energies of each of the compounds were calculated from $E = 28.635/\lambda(\text{nm})$. Thus, the wavelength of interest is that where the emission spectrum first leaves the baseline. These wavelengths, and the energies corresponding to them, are shown in Table III as λ_s and E .

It can be seen that the energies of emission fall in the range of 66–78 kcal/mole. From studies of other brominated flame retardants,^{14–21} it is believed that bromine-containing flame retardants thermally decompose by homolytic cleavage of the aromatic C—Br bond, which has a bond energy in the 72–80 kcal/mole range. Assuming that these compounds, incorporated in polymers either as additives or “comers” may degrade photolytically in a similar manner, the emission energies are of the same order of magnitude as the bond dissociation energy of an aromatic C—Br bond.

CONCLUSIONS

If the reported brominated aromatic compounds decompose through the homolytic cleavage of one or more of the C—Br bonds, the calculated phosphorescence emission energies 66–78 kcal/mole may give suitable screening values for potential fire retardants.

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Received October 18, 1979
Accepted February 21, 1980