

A New Mechanism of Flame Retardancy for Polyurethanes

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Synopsis


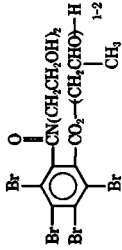
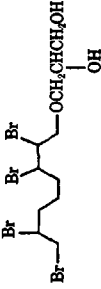
A chemical model is outlined which gives a simple description of flame-retardant efficiency of organic bromides in flexible polyurethane foam systems. The mechanism suggests dehydrobromination by an interplay of S_N1 and S_N2 reactions in intramolecular and intermolecular processes. Evidence is presented to demonstrate that flame-retardant efficiency is directly related to the facility of dehydrohalogenation by an intramolecular process in which cyclic urethanes (five to ten membered rings) are formed by either S_N1 and/or S_N2 reactions. The requirement for a nucleophile, such as carbamate nitrogen, in halogen systems is suggested. In other mechanistic aspects, it was shown that flame retardancy passes through a maximum as a function of bromide content in the foam. It is believed that this behavior reflects certain undefined combustion aspects in the solid phase. It is also shown that unlike additive flame retardants, the TGA's of neither the starting bromine-containing alcohols nor their model N-phenyl-carbamates correlate with the weight loss curves of the control foam. Instead, the TGA's of both flame retardant and nonflame-retarded foams from the reactive bromide alcohols all fall in about the decomposition range of the control foam. As a practical consequence of the results reported herein, it is now possible to correlate flame retardancy and structure as well as formulate new flame retardants with greater assurance of success.

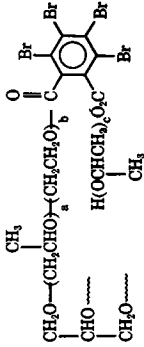
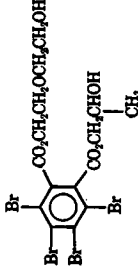
INTRODUCTION

Several mechanistic routes have been offered to explain the flame-retarding action of organic bromides in various polymeric systems.¹⁻⁴ All theories of necessity involve the formation of hydrogen bromide prior to flame extinguishment. For example, the most commonly cited mechanism² provides much evidence for hydrogen bromide as the terminator for propagating free radicals formed at flame temperatures.

Despite numerous investigations of the flame retardancy of polymers with organic halides, little is known with certainty about the mechanism of formation of hydrogen halide in a flame. The literature is replete with examples which generally assume dehydrohalogenation by a thermochemical homolytic elimination process.⁵⁻⁸ Thus, the influence of bromide structure on flame-retardant efficiency has been inferred from correlation of qualitative considerations of carbon-bromine bond strengths of model compounds and performance in polymeric systems.⁹⁻¹¹

TABLE I
Compositions Investigated

Compound number	Compound name	Structure	mp, °C	η_{sp} , cps	% Br found	General comments
1	3,4-Dibromocyclohexane-1,1-dimethanol		127.5-129	—	53.29	insoluble in LG-56
2	Brominated product of the propylene oxide/allyl glycidyl ether adduct of glycerin	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{O}-\text{CH}_2-\text{CHO}-(\text{CH}_2\text{CHO})_5-\text{H} \\ \\ \text{CH}_2\text{OCH}_2\text{CHCH}_2\text{Br} \\ \\ \text{Br} \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CHO}-(\text{CH}_2\text{CHO})_c-(\text{CH}_2\text{CHO})_d-\text{H} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{OCH}_2\text{CHCH}_2\text{Br} \\ \\ \text{Br} \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{O}-\text{CH}_2-\text{CHO}-(\text{CH}_2\text{CHO})_f-\text{H} \\ \\ \text{CH}_2\text{OCH}_2\text{CHCH}_2\text{Br} \\ \\ \text{Br} \end{array}$	—	1900	16.69	—
3	Propylene oxide adduct of TBPA/DEA		54-74	—	50.64	Glassy, brittle solid
4	β,γ -Dihydroxypropyl 2,3,7,8-tetrabromooctyl ether		—	126,600	58.71	highly compatible with variety of reagents

5	1,2,5,6-Tetrabromo-3,4,-di-hydroxyhexane	$\begin{array}{c} \text{Br} & & \text{Br} \\ & & \\ \text{Br}-\text{CH}_2-\text{CH} & \text{CH} & \text{CH}-\text{CH}_2-\text{Br} \\ & & \\ \text{OH} & & \text{OH} \end{array}$	isomer A, 171.5- 172.5 isomer B, 98-99	72.41	two isomers isolated
6	Propoxylated product of TBPA/NIAX Polyol LC-60 adduct	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{O}-\text{CH}_2-\text{CHO}-(\text{CH}_2\text{CH}_2\text{O})_b-\text{C} \\ \quad \quad \quad \quad \quad \quad \\ \text{CHO} \quad \quad \quad \text{H}(\text{OCHCH}_3)_a\text{OC} \\ \quad \quad \quad \\ \text{CH}_2\text{O} \quad \quad \quad \text{CH}_3 \end{array}$ 	1832	11.91	—
7	Dibromoneopentyl glycol	$\begin{array}{c} \text{HOCH}_2 & & \text{CH}_2\text{Br} \\ & & \\ \text{C} & & \text{C} \\ & & \\ \text{HOCH}_2 & & \text{CH}_2\text{Br} \end{array}$	109-110	61.00 (calcd.)	Procured from Dow Chem. Co.
8	<i>trans</i> -2,3-Dibromo-2-butene-1,4-diol	$\begin{array}{c} \text{HOCH}_2 & & \text{Br} & & \text{CH}_2\text{OH} \\ & & & & \\ \text{C} & & \text{C} \\ & & \\ \text{Br} & & \text{Br} \end{array}$	113-115	65.00 (calcd.)	Procured from GAF Corp.
9	2,3-Dibromopropanol-1	$\begin{array}{c} \text{Br} & & \text{Br} \\ & & \\ \text{Br}-\text{CH}_2-\text{CH} & \text{CH}_2-\text{OH} \end{array}$	bp 219 dec./ 760 mm	73.40 (calcd.)	Procured from Michigan Chem. Corp.
10	Firemaster PHT4-Diol		7500/50°	46.00 (calcd.)	From Michigan Chem. Corp.

The purpose of this paper is to present evidence for a new mechanism of dehydrobromination of flame-retarded polyurethane flexible foams which possess bromine as part of the polymer structure. In addition, an explanation is given for the wide variation of bromine concentration needed to give the same level of flame retardancy in other polymer systems.

EXPERIMENTAL

The flame retardant reagents used in this study were bromine-containing polyols having different structural features in the vicinity of the carbon-bromine bonds. The majority were synthesized by adding elemental bromine to the corresponding olefin-alcohols. Synthetic procedures for the new compositions are given below and structure and properties for all reagents are summarized in Table I.

Preparation of Flame-Retarding Reagents

3,4-Dibromocyclohexane-1,1-dimethanol (1). 3-Cyclohexene-1,1-dimethanol (710 g, 5.0 mole), and 5 liters chloroform were placed in a 2-liter, four-necked flask fitted with a Trubor stirrer, thermometer, condenser, and dropping funnel and wrapped with aluminum foil to protect the contents from light. Bromine (799 g, 5.0 mole) dissolved in 1 liter chloroform was added dropwise during 4 hr while maintaining the reaction mixture at 0°. The reaction mixture was allowed to warm to ambient temperature while standing overnight. The crude white product was collected by filtration washed with 3500 ml chloroform and dried; yield 1168 g (78%), mp 99–105°. Recrystallization from 3.5 liters hot ethanol afforded 932 g (62%) pure product, mp 127.5–129°.

ANAL. Calcd. for $C_8H_{14}Br_2O_2$: C, 31.82; H, 4.67; Br, 52.92. Found: C, 31.93; H, 4.77; Br, 53.29.

Brominated Propylene Oxide Adducts of 3-Cyclohexene-1,1-dimethanol.

Preparation of the starting propylene oxide adducts of 3-cyclohexene-1,1-dimethanol was carried out in accordance with well-known procedures for alkoxylation of alcohols with olefin epoxides. The liquid oxypropylated adduct of this example possessed an average molecular weight of 192, calculated on the basis of the hydroxyl number which, in turn, was found to be 584. The average number of moles of propylene oxide per mole of 3-cyclohexene-1,1-dimethanol is, therefore, 0.86.

The 0.86 mole propylene oxide adduct of 3-cyclohexene-1,1-dimethanol (760 g, 3.96 mole) and 1000 ml chloroform were placed in a dry 5-liter, four-necked flask fitted with a Trubor stirrer, thermometer, condenser, and dropping funnel. The reaction mixture was protected from light by wrapping aluminum foil around the flask. Bromine (627 g, 3.92 mole) dissolved in 500 ml chloroform was added to the stirred reaction mixture over a period of 4 hr while maintaining the temperature at -5° to 0°C . The reaction mixture was exothermic and cooling was necessary throughout the

addition of bromine. The yellow-brown liquid reaction product was allowed to warm to ambient (25°C) temperature on standing overnight. In order to lower the acid number (25.4), the reaction product was treated with five 100-g batches of strongly basic anion exchange resin (Amberlite IR-900) to remove bromide ion. This treatment lowered the acid number to 0.387. The ion exchange resin was then removed by filtration and the filtrate freed of solvent by heating at 46°C and 4 mm mercury pressure for 1 hr. The brominated residue product (yield 1183 g, 85%) of the 0.86 mole propylene oxide adduct produced in accordance with this example has the following characteristics:

Acid number, mg KOH/g	2.30
Hydroxyl number, mg KOH/g	
found	274.5
calcd.	318.5
Bromine, %	
found	41.72
calcd.	45.50
Brookfield viscosity (25°C), cps	147,000

Propoxylated Adducts of Glycerin Containing β,γ -Dibromoallyloxy-methyl Pendant Groups (2). To 4000 g (1.11 mole) unsaturated (1.248 mg KOH/g) polyol (prepared from the reaction of a mixture of allylglycidyl ether and propylene oxide on glycerin by the standard procedure for foam polyols) dissolved in 1500 ml methylene chloride was added 717 g (4.48 mole) bromine in 800 ml methylene chloride dropwise during 4.5 hr while maintaining the reaction temperature at 15–20°C. A positive nitrogen pressure was employed during the addition and the reaction contents were protected from light. The resulting light-red liquid was passed through a Roto Film molecular still at 80° and 760 mm and once again at 80° and 25–30 mm. The resulting dark-brown liquid (4562 g) analyzed as follows:

Bromine, %	16.69
Hydroxyl number, mg KOH/g	44.50
Acid number, mg KOH/g	4.61
Unsaturation, meq/g	0.210
Brookfield viscosity (25°C), cps	1900
Gardner color	13

Tetrabromophthalic Anhydride (TBPA)/Diethanolamine/Propylene Oxide Amide-Ester Adducts (3). To a slurry of 1856 g (4.0 mole) TBPA in 2500 ml xylene maintained at 115–120°C was added dropwise, but intermittently with propylene oxide, as described subsequently, a total of 425 g (4.0 mole) diethanolamine. When one half of the DEA had been added, the thick reaction slurry was stirred for 1 hr and 150 g propylene oxide was added to facilitate stirring. The propylene oxide reacted instantaneously as judged by the lack of reflux, and the remainder of the DEA was added dropwise. The addition of DEA took a total of about 1.5 hr. When the addition of DEA was complete, propylene oxide was then added dropwise to the reaction mixture while maintaining the temperature at 115–120°C.

Acid number determinations were made of reaction mixture aliquots at regular intervals until a value of less than 0.50 was obtained. A good indication of complete reaction was obtained when propylene oxide reflux had commenced. A total of 427 g (7.36 mole) propylene oxide was required. At this point, the reaction mixture consisted of two separate liquid phases. The product was allowed to stand for three days in a separatory funnel and the two layers separated. The viscous (η_{sp} , 103,600 cps) product layer (yield 2250 g, 83%) was freed of volatiles by passing through a falling film still at 115°C and 20 mm pressure to give a glassy solid residue product, yield 1764 g (65%). The properties of this product are shown below.

Br, %	
found	50.64
calcd. for $C_{15}H_{17}Br_4NO_6$	
(where $n = 1$)	50.98
calcd. for $C_{18}H_{23}Br_4NO_7$	46.66
(where $n = 2$)	
Hydroxyl number, mg KOH/g	
found	246
calcd. for $C_{15}H_{17}Br_4NO_6$	268.5
calcd. for $C_{18}H_{23}Br_4NO_7$	245.7
Acid number	nil
Melt temp., °C	57-74

β,γ -Dihydroxypropyl 2,3,7,8-Tetrabromooctyl Ether (4). To the starting diol, 2,7-octadien-1-yl 2,3-dihydroxyprop-1-yl ether (108 g, 0.54 mole), in 100 ml carbon tetrachloride at 0°C was added a solution of 172.5 g (1.08 mole) bromine in 100 ml carbon tetrachloride while maintaining the temperature at -4° to 0°C and protecting the reaction setup from light by means of aluminum foil. When one half the bromine solution had been added, another 100 ml carbon tetrachloride was added to the reaction mixture to lower the viscosity. The addition took 4.5 hr. When the addition was complete, the reaction mixture was allowed to warm up to ambient temperature on standing overnight. The resultant two-phase, light-orange, liquid product mixture was then subjected to reduce pressure (6.0 mm) at 50°C for 1 hr to remove volatile components. No evidence of HBr by a moist litmus test was noted at this point. The residue product gave the following properties:

Brookfield viscosity (25°C), cps	126,600
Hydroxyl number, mg KOH/g	185.15
Acid number, mg KOH/g	16.45
Bromine, %	
found	58.71
calcd.	61.50
Solubility, 1 part compatible in	
3 parts of LG-56	

To lower the acid content, the product was taken up in chloroform and the chloroform solution washed with three 100-ml portions of saturated sodium bicarbonate solution, then with four 100-ml portions of distilled

water. After drying over anhydrous magnesium sulfate, the chloroform was removed at 50°C and 3 mm to yield a yellow liquid, acid number 0.412 mg KOH/g.

1,2,5,6-Tetrabromo-3,4-dihydroxyhexane (5). The two isomeric derivatives of **5** (mp 171.5–172.5°C and 98–99°C) were synthesized by the method given in previous published work.^{12,13} Except as noted, the results included in this study are based on the high-melting isomer.

Propoxylated Product of TBPA/Polyol Adduct (6). Sodium acetate (2.4 g) and 3000 g (1.0 mole) NIA X Polyol LC-60 (an alkylene oxide adduct of glycerin containing largely primary hydroxyl endgroups with hydroxyl number about 60 mg KOH/g) was placed in a previously dried 5-liter, four-necked flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser. The contents of the flask were kept under a positive pressure of dry nitrogen and heated to 100°C. Tetrabromophthalic anhydride (576 g, 0.535 mole) was added portionwise during 25 min, and then 2.1 g stannous octoate was added. The reaction mixture was heated for 5 hr at 100°C after which propylene oxide was added until the oxide commenced to reflux; uptake, 74 g (1.22 mole). The reaction mixture was then heated at 83° and 1 mm pressure to remove volatile components. Analysis revealed the following properties:


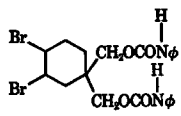
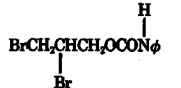
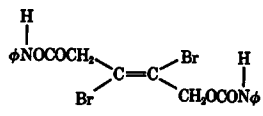
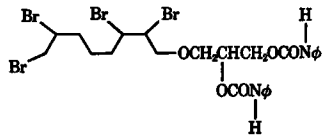
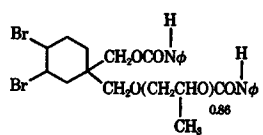
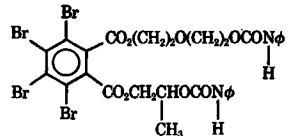
Bromine, %	11.91
Hydroxyl number, mg KOH/g	42.80
Acid number, mg KOH/g	0.337
Viscosity (25°C), cps	1832
Gardner color	1

Preparation of Model N-Phenylcarbamates

Reaction of Brominated Alcohols with Phenyl Isocyanate. These products are given in Table II. The general procedure employed for these reactions is illustrated by the reaction of dibromoneopentyl glycol with phenyl isocyanate. Dibromoneopentyl glycol (1087 g, 415 mole) was added portionwise over 2 hr to 988.5 g (8.3 mole) phenyl isocyanate with stirring while keeping the temperature of the exothermic reaction at 69–84°C by means of a cold water bath. As indicated in Table II, a few reactions were run in a solvent. When the alcohol addition was complete, the reaction mixture was stirred at 84°C for 1 hr, at which point the mass solidified. The white, solid reaction product was dissolved in 2100 ml hot toluene and maintained at 111°C for 1 hr with stirring. After cooling, the crude, white solid product was collected by filtration and dried to yield 2087 g (100%), mp 147.5–149°C. An analytical sample was prepared by recrystallizing 40 g of the crude product twice from toluene; yield 33 g (83%), mp 149–150°C.

In four runs of Table II, the products were characterized as nondistillable, noncrystallizable solids and were employed directly in the TGA studies. These residue products were freed of volatiles by heating for 1 hr at 85° and 4.0 mm pressure. For the elemental analysis and TGA studies, the

TABLE II
 Conversion of Bromine-Containing Alcohols to Corresponding

Carbamate structure	Rxn. Conditions				
	Alcohol, moles	Phenyl isocyanate, moles	Reaction solvent	Yield, %	mp, °C
$(\text{BrCH}_2)_2\text{C}(\text{CH}_2\text{OCN}\phi)_2$ 	4.15	8.30	Neat	100	149-150
	0.673	1.34	dimethoxy ethylene glycol	100	62-80
$\text{BrCH}_2\text{CH}(\text{Br})\text{CH}_2\text{OCN}\phi$ 	1.28	1.285	neat	59.3	79-81
	1.19	2.41	neat	72.1	187-188
	0.101	0.202	toluene	94	—
	0.26	0.52	toluene	95.6	52-66
	0.234	0.468	toluene	100	53-66

samples were treated further by subjecting 5 g samples, placed in a Petri dish, to 80°C and 4 mm mercury pressure in a vacuum oven for 64 hr.

Foaming Procedure

Flexible foams used in this study were produced in 14 × 14 × 6-in. cardboard boxes using the standard one-shot handbatch technique based on 500 g polyol. Formulations were standardized as follows (in parts by weight): NIAX Polyol LG-56, 100; water, 4; silicone surfactant, 0.5; NIAX

N-Phenyl Carbamates with Phenyl Isocyanate

Recryst. solvent	Analyses								Product description
	Carbon		Hydrogen		Nitrogen		Bromine		
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
toluene	45.62	45.44	4.03	5.60	5.60	5.08	31.95	32.46	white crystals
residue product	48.91	49.18	4.48	4.62	5.19	5.16	29.58	29.49	brown glass
toluene	35.64	36.18	3.29	3.13	4.16	4.47	47.42	43.81	white solid
toluene and ethanol	44.66	44.35	3.33	3.40	5.79	5.82	33.01	33.37	tan solid
residue product	39.61	38.78	3.99	4.00	3.70	3.34	42.16	42.82	black, tacky product
residue product	50.02	50.87	4.98	5.26	4.75	4.49	27.08	26.65	brown glass
residue product	40.21	41.71	3.03	3.46	3.23	3.18	36.90	34.17	cream- colored glass

Catalyst A-1, 0.1; NIAX Isocyanate TDI, varied; stannous octoate, varied; and isocyanate index, 105. The blend of flame retardant and polyol, surfactant, and isocyanate was weighed into a $\frac{1}{2}$ -gallon container, fitted with a baffle, and stirred for 60 sec with a high-speed stirrer at 2700 rpm. The mixture was allowed to stand for 15 sec, and then stirring was continued for another 15 sec. During the 15-sec stirring period, but after 5 sec had elapsed, a solution of the NIAX Catalyst A-1 in the water was added, and after 10 sec the stannous octoate was added from a syringe. When the 15-sec stirring was complete, the mixture was quickly poured

into the mold, whereupon the mass foamed. The cream and rise times were recorded. The foams were allowed to stand at ambient laboratory conditions for two days before testing.

Testing Procedure

Flame retardance was tested by standard ASTM D-1692-67T and oxygen index (ASTM D-2863-70) methods. Conventional foam sample size specified by ASTM D-1692-67T ($2 \times 1/2 \times 6$ in.) was employed in the oxygen index test. The oxygen index numbers represent an average of three determinations on fresh samples. Each foam sample was crushed and equilibrium attained in the oxygen index device by allowing the sample to stand 2-3 min before testing. Standard ASTM procedure was also followed for dry heat aging and humid aging (ASTM D-1564) of foam specimens.

RESULTS AND DISCUSSION

A series of bromine-containing alcohols were studied for their flame-retarding efficiency when incorporated as part of the polymer in flexible urethane foams. Structural types of flame retardant reagents were diverse, and a broad range of bromine concentrations in the foams was studied.

The hydroxyl numbers and the type of alcoholic functionality varied for the reagents. It was possible to make foams from all the reagents used although they differed somewhat in ease of processing.

Thermogravimetric Studies

For a fuller investigation of the stability of the foams to heat, DTA and TGA data in air were recorded for some foams as well as TGA's for the flame-retardant reagents themselves and their model carbamate derivatives. The plots are shown in Figures 1 through 4, respectively. The TGA results of Figure 1 show that the well-known characteristic lowering of decomposition temperature of both flame-retarded flexible¹⁴ and rigid¹⁵ foams by reactive phosphorus compounds is not extended to foams with incorporated bromine derivatives. Interestingly, the DTA's exhibited three transitions for the control foams as well as for the nonflame-retarded foam containing an aromatic bromide (compound 10). Surprisingly, however, with all the flame-retarded foams only one transition is seen. This could indicate a change in the mechanistic course of degradation of the flame-retarded polymeric systems. For example, it could imply a mechanism of action of bromo compounds in the solid state during the combustion process. Evidence implicating bromides in effectively inhibiting the pyrolysis of polyurethane¹⁶ and of polyethylene¹⁷ in the condensed phase have been recently reported.

Investigations of TGA of polyurethane foams flame retarded with additive-type reagents have led several groups of workers^{18,19} to suggest that the decomposition range of the most effective flame retardants are in the same temperature range of degradation of the foam itself. On this basis,

Bromide	Bromine, %	DTA Peak (a)		TGA, °C. (b)		
		Temp., °C	Type	Weight Loss at		
				10%	25%	50%
Control	0	274, 298, 330	Exo	284	304	325
<chem>BrC1CC(O)CC1O</chem>	2.33	311	Exo	279	298	310
<chem>BrC1CC(O)C(Br)C(O)C1O</chem>	2.57	310	Exo	283	305	322
<chem>BrC1CC(O)CC1O</chem>	2.45	311	Exo	289	309	325
<chem>BrC1CC(O)C(Br)C1O</chem>	2.53	308	Exo	285	301	285
<chem>BrC1C(C(=O)OCCO)C(Br)C(C(=O)OCCO)C1Br</chem>	2.57	293, 318, 356	Exo	279	300	317

Foam Formulation: NIAX Polyol LG-56, 100; Water, 4.0; A-1, 0.10; stannous octoate, Varied; L-540, 0.50; TDI, Varied; Index, 105. Foam Density; 1.5 lb./ft.³

(a) Airflow, 10 cc/min.; temp. rise, 8°C/min.

(b) Airflow, 10 cc/min.; temp. rise, 10°C/min.

Fig. 1. Volatility and thermal stability of some flexible polyurethane foams containing bromide flame retardant.

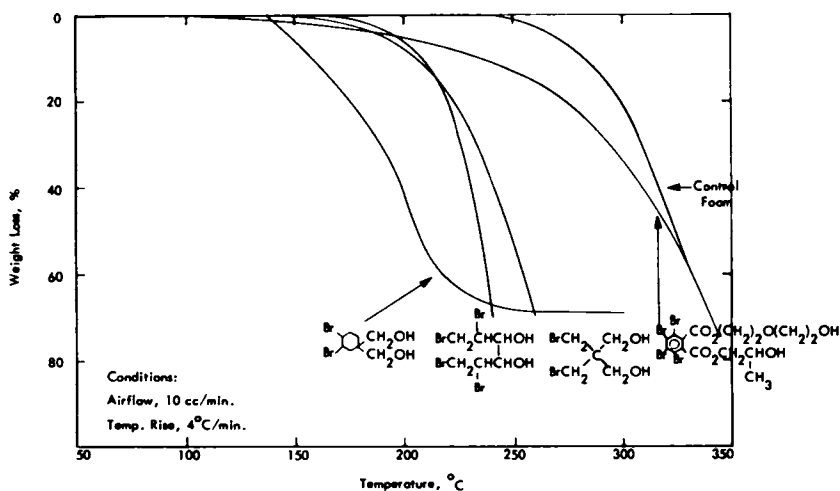


Fig. 2. TGA analysis of various bromide diols.

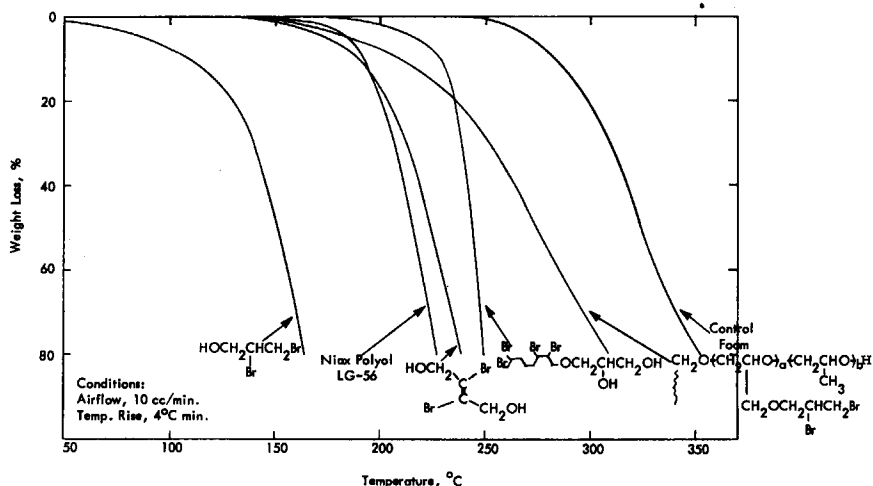


Fig. 3. TGA analysis of various bromine-containing alcohols.

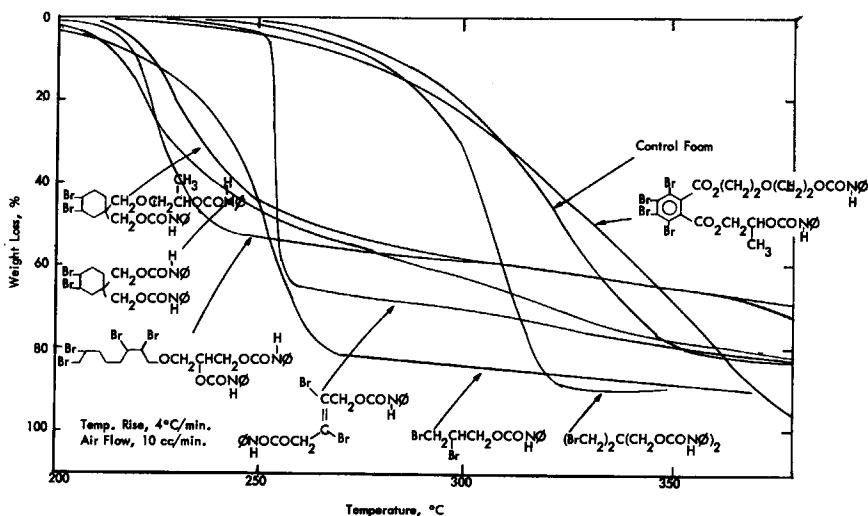


Fig. 4. TGA analysis of various phenyl carbamates.

the additive approach traditionally matches TGA's of the flame-retardant reagent and foam. By contrast, the weight loss-versus-temperature plots of the brominated alcohols of this study, illustrated in Figures 2 and 3, show that such data do not reveal clues to the predicted flammability behavior of reactive flame-retardant intermediates. In fact, one of the least effective reagents (10) exhibited decomposition most nearly like the foam.

In an effort to gain a more realistic insight into correlations of TGAs of reactive flame retardants with the foam, model *N*-phenyl carbamates similar in chemical structure and reactivity to those present in the foam polymer were prepared and their TGA's determined. These TGA data

are shown in Figure 4. The results show that like the alcohols, the carbamates also do not exhibit a weight loss correlation with that of the foam. In most cases, the carbamates lose weight at a slightly higher ($\sim 10^\circ\text{C}$) temperature. Undoubtedly, TGA of reactive flame retardants do not afford a basis for predicting effectiveness in foams.

Flammability Results

Oxygen indexes of foams containing the various bromides listed in Table I are plotted against bromine content in Figure 5. Flammability classification according to ASTM D-1692-67T is given in Table III. The self-

TABLE III
Effect of Ring Size on Flammability by ASTM D1692-67T

Ring size	Compd. no.	Burning extent, in.						
		Bromine in foam polymer, %						
		1.0	1.5	2.0	2.5	3.0	3.5	4.0
5	9	—	B	2.6	2.1	1.9	1.9	1.8
5	5	—	B	B	3.5	1.9	2.0	2.1
5	8	—	B	B	B	B	B	3.9
6	7	—	B	3.4	B	3.8	2.4	2.4
7	1	—	B	B	3.4	2.3	2.4	2.7
8	4	B	2.4	2.2	2.2	1.9	1.5	1.4
9(7)	3	—	B	—	—	4.0	—	2.3

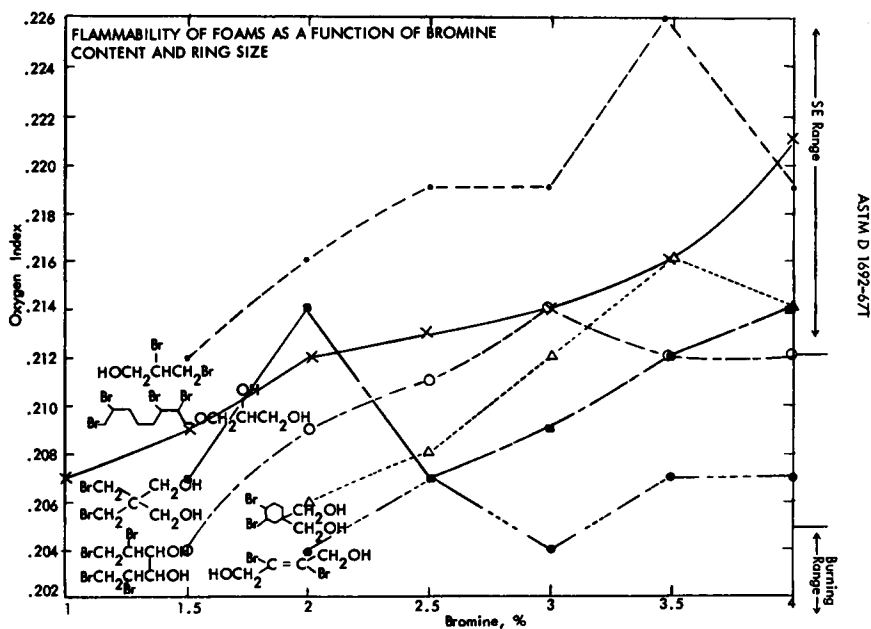


Fig. 5. Flammability of foams as a function of bromine content and ring size.

extinguishing and burning ranges by the ASTM procedure are also given in Figure 5. Between these two ranges, a "gray area" exists where either SE or burning (B) ratings were obtained. From this, it can be concluded that foams possessing excellent flame retardancy generally have oxygen indexes of 0.212 or higher, while values between 0.207 and 0.212 are borderline.

With the exception of compounds **2**, **6**, and **10**, all the reagents of this study effectively improved the fire resistance of urethane foams. Compounds **2**, **6**, and **10** were classified as burning up to 5% contained bromine in the foam polymer (based on bromine reagent, polyol, and isocyanate content).

The curves of Figure 5 show that most plots pass through a maximum in flame retardancy as a function of the per cent of bromine. Furthermore, the bromine concentration varies at the peak maximum for the individual compositions but generally occurred in the range of 2% to 3.5%. The cause of this behavior is considered in a later section.

Correlation of Flame Resistance with Bromide Structure

Examination of the results of Figure 5 and Table III suggest that flame resistance could be significantly related to the structure of the reactive bromide intermediates of this study. It is proposed that a mechanism for HBr generation in these polyurethane systems involve favored intramolecular substitution by cyclic processes which proceed via carbonium ion (S_N1) and/or bimolecular (S_N2) reactions. By this means, the effectiveness (efficiency) of brominated polyols is directly dependent on the ease with which HBr is formed in ionic displacement reactions in which the urethane nitrogen behaves as a nucleophile. Processes which do not favor an intramolecular scheme would require a less favorable intermolecular substitution. The latter route would result in a more flammable polyurethane.

Table III shows that although the differences are not large by the flammability test methods employed, maximum flame retardance by an intramolecular process was achieved in those cases where five-, six-, and seven-membered rings were favored (eight-membered rings represent a special case considered below). On the other hand, compositions which required the formation of very large rings, such as in the case of compound **2**, did not render their foams flame retardant. Examination of the data show that within a particular ring series, such as the three instances involving five-membered intermediates, the ease of HBr formation reflect the stability of the particular bromine atom toward displacement. Thus, as expected, the vinyl bromide of **8** exhibited low effectiveness. To a lesser extent, the steric hindrance of **5** to backside attack forced the meso modification to proceed by S_N1 as well as S_N2 , thereby exhibiting less flame retardancy as compared to compound **9** which, in turn, must proceed entirely by the more facile S_N2 process under our conditions. Similarly,

compound **1** is more effective than **7** because it is capable of undergoing both displacement processes while **7** can only occur via S_N1 .

It is well known that compounds containing aromatic bound bromine atoms are not alone good flame retardants, especially in flexible foams. For example, compound **6** was completely ineffective while **10** was very inefficient at rendering foams flame retardant. Unexpectedly, **3** exhibited active flame retardancy (2.3 in. at about 4.0% Br) for an aromatic bromide. This will be considered in further detail in a later section.

On special interest are the results obtained with β,γ -dihydroxypropyl 2,3,7,8-tetrabromooctyl ether (**4**). It is believed that the permanence of flame retardance of foams after dry heat and humid aging prepared with this derivative further supports the thesis that dehydrobromination occurs by intramolecular S_N1 and S_N2 reactions rather than by thermal free-radical eliminations as it was previously regarded.⁶ It is reasoned that substitution reactions with **4** involve the formation of HBr by a slower heterocyclization process since eight- and nine-membered rings are required. Additionally, because the side chain segment of **4** (ten-atom pendant chain with bromine bound to the last two atoms) would have greater mobility in flexible polymer, the probability of alkylations by intermolecular reactions involving both urethane and urea nitrogens in the polyurethane would be increased. Thus, insofar as only 50% of the bromine content of **4** can undergo intramolecular reactions to give eight- and nine-membered rings, this could explain its unexpected high flame-retardant efficiency.

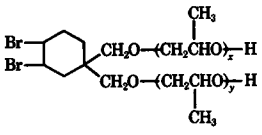
Compound **2** represents another case where only intermolecular reactions are feasible. However, unlike **4** it appears that the restricted side chain flexibility (five-atom pendant chain with bromine bound to the last two carbon atoms) renders its foams nonflame retarded. Thus, it would appear that side-chain length is important in intermolecular interactions.

Effect of Ring Size on Flammability. Figure 6 and Table IV present oxygen index and ASTM D-1692-67T flammability data, respectively, for various propylene oxide adducts of 3,4-dibromocyclohexane-1,1-dimethanol (**1**). The results show very dramatically the high effectiveness of the reagents which can form seven- or eight-membered rings ($x + y = 0.86$). With the other bromide derivatives, which require at least a ten-membered ring formation, SE foams were not provided at comparable bromine concentrations. Further support is gained from the fact that oxide adducts of dibromoneopentyl glycol are also less efficient than the parent compound in rendering flexible urethane foams flame retardant. The large OI values for **1** as compared to its derivative ($x + y = 0.86$) is not clear but may be related to different effectiveness from the various possible stereoisomeric forms.

Flame Retardancy with Aromatic Systems. As mentioned previously, compounds containing bromine bound to an aromatic nucleus are not efficient flame retardants. This usual behavior of aromatic bromine compounds is not unexpected when flame retardancy is related to the ease of

hanced flame retardancy. This behavior is facilitated in **12** by the formation of nine-membered cyclic derivatives in which case alkylations occur more readily on the highly nucleophilic urea functionality as compared to urethane.

TABLE IV
Effect of Chain Length (Ring Size) on Foam Flammability by ASTM D-1692-67T

	Bromine, %	Inches burned
Where $x + y = 0.86$	1.5	3.8
	2.0	3.5
	2.5	3.4
	3.0	2.9
	3.5	2.1
	4.0	2.1
	4.5	2.1
Where $x + y = 2.05$	1.5-4.0	burned
Where $x + y = 3.96$	1.5-4.0	burned
Where $x + y = 5.39$	1.5-4.0	burned

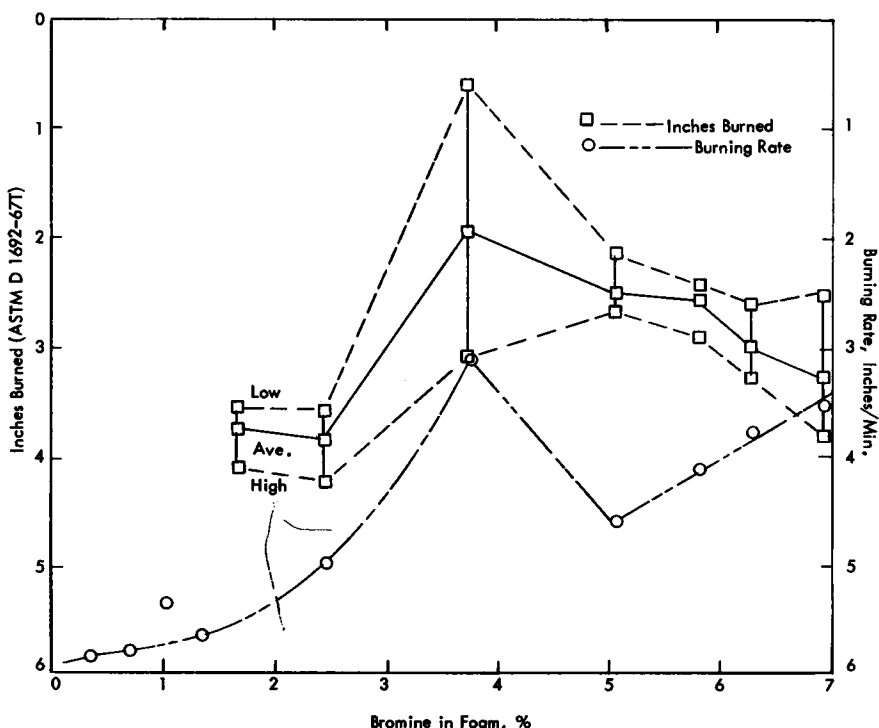


Fig. 7. Flammability resistance of flexible foams containing 3,4-dibromocyclohexane-1,1-dimethanol.

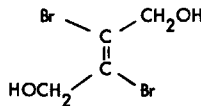
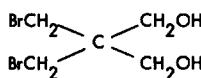
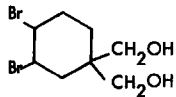
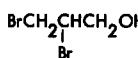
Compound Number	Flame Retardant Structure	Scorch (Discoloration) Rating	Oxygen Index
--	Control (No Additive)	0	0.177
8		0	0.207
7		1	0.207
1		2	0.208
9		4	0.219

Fig. 8. Comparison of foam scorching (discoloration) for different brominated alcohols at 2.50% Br.

Effect of Nucleophiles on Halogen-Containing Flame Retardants. The overall results of the work described herein and, in particular, the flammability data obtained for compound **3** versus those seen for **2**, **6**, and **10** suggest requirement of a nucleophile for flame-retarding polyurethanes with halogens. The presence of nitrogen nucleophiles in flame-retarding polyurethane systems would explain their lower requirement for bromine as compared to substrates lacking strong nucleophiles, for example, polyesters and epoxide polymers.

Influence of Bromine Concentration. Other mechanistic aspects of flammability are implicated from the results presented in Figures 5 and 6 and Table III. The data show that certain flame-retarding reagents cause flammability resistance of foams to pass through a well-defined maximum with increasing concentration of bromine. In addition, the maximum peak varies with the reagent employed. Figure 7 exemplified the trend more dramatically, where foams bearing as high as 7% bromine from compound **1** were successively prepared and evaluated. Rigid polyurethane foams possessing phosphorus are well known to pass through a maximum in flame retardancy at 1.5%, phosphorus,⁶ but similar behavior with halides has not been previously reported. Inasmuch as phosphorus compounds act wholly in the solid phase,⁶ it would appear that formation of a maximum in flame retardancy could be general for reagents which are involved in combustion of the solid fuel rather than in quenching reactions in the flame. This interpretation receives further support from the fact that polyesters containing both phosphorus and bromine compounds give an indication of passing through a maximum as a function of concentration by ASTM D-757 flame test.²⁰ Undoubtedly, pyrolysis of the polymeric fuel, especially at

TABLE V
Properties of Foams Containing About 3 per cent Bromine from the Various Bromides

Compound number	Control	1	2	3	4	5	6	7	8	9	10
Bromine	0%	2.45%	3.00%	3.10%	3.00%	3.23%	3.00%	2.99%	3.03%	3.21%	3.13%
Density, pcf	1.56	1.58	1.45	1.67	1.63	1.55	1.54	1.66	1.64	1.56	1.60
Air porosity, ft ³ /min/ft ²	117	103	31	—	94	113	96	59	148	73	12
Tensile strength, psi	14.2	16.2	8.8	13.5	13.0	16.1	15.7	18.5	—	15.1	20.2
Elongation, %	158	203	165	97	142	218	169	188	—	184	218
Tear resistance, lb/in.	2.26	2.48	1.21	—	2.21	2.35	2.17	2.65	—	2.56	3.03
4-Inch ILLD, lb/50 in. ²											
25% deflection	35	34	20	46	39	31	38	38	31	37	43
65% deflection	64	67	37	86	73	60	67	73	58	66	80
25% return	24	20	14	31	25	20	25	24	21	24	26
Return value	69	60.4	71	67.0	65	65	66.6	63.4	66	65	59.3
Load ratio	1.86	1.98	1.84	1.90	1.88	1.95	1.75	1.91	1.85	1.81	1.85
90% Compression set, %	4.7	21.7	8.6	8.4	5.1	10.8	4.2	14.4	—	7.5	74.3

the solid-gas interface, is essential in providing gaseous fuel for propagation combustion. On this basis, it is suggested that bromine compounds, in particular HBr, initially act to alter the rate of pyrolytic reactions of the polymer by free-radical processes so that less flammable gaseous products are formed, whereas excessive pyrolysis to smaller, more flammable degradative species result as the bromine concentration is increased beyond a certain critical limit.

Scorching

In a series of experiments involving several reagents, we studied the correlation between scorch and the resistance toward displacement of the different brominated derivatives. Degree of discoloration was estimated from visual observation of vertical cross sections of large (2 ft × 2 ft × 2 ft) flexible foam buns by a color rating system of 0 (no discoloration) to 5 (severe discoloration, brown). The results of this study are shown in Figure 8. The data show that compound **9** produces severe scorch when compared with the other bromine derivatives. Evaluations also showed scorching tendency to diminish as the bromine is more difficult to displace.

Physical Properties of Flame-Retarded Foams

Physical properties of flexible foams containing about 3% bromine from the various bromine alcohols of this study are shown in Table V. A comparative control foam without an added flame retardant is also shown. Although in specific comparisons some marked differences in overall properties are seen, generally speaking the halogenated derivatives produced foams with slightly lower porosity and somewhat greater load-bearing properties and tensile strengths. Perhaps most notable are the slightly higher 90% compression sets for the majority of the foams. These results strengthen the notion that brominated materials can conceivably afford the property balance needed to serve as creditable flame retardants.

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