Studies on Nitroaniline–Sulfuric Acid Compositions: Aphrogenic Pyrostats

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Synopsis

Nitroaniline–sulfuric acid compositions, a source of a new class of aphrogenic pyrostats (intumescent fire-quenching agents) have been studied. Thermogravimetric analysis of the compositions and their expansion products was carried out. The chemical compositions of the foams were determined, and considerable similarity was noted. Sulfur is present exclusively as sulfonic acid groups. Appreciable deamination occurs during expansion, particularly at higher acidic content. Sulfur dioxide and water are major gaseous constituents. Only 2- and 4-nitroanilines can be converted into voluminous foams; they behave like difunctional monomers. 3-Nitroaniline expands only slightly into brittle products; it acts like a trifunctional monomer.

INTRODUCTION

An aphrogen is a substance that will convert into a foam or sponge on heating, in particular, a material that after initiation develops spontaneously into a foam or sponge. A pyrostat is a substance that quenches a fire. Thus, an aphrogenic pyrostat is an intumescent fire-quenching substance. The discovery that a wide variety of nitroanilines can be converted into foams of low density and excellent fire resistance and that nitroanilinium sulfates and nitroanilinesulfonic acids have fire-retardant qualities encouraged further study of the thermolytic reactions of nitroaniline–sulfuric acid compositions.

The purpose of this work, concerned with the three isomers of nitroaniline, was threefold: first, to ascertain what reactions occur on heating before expansion ensues and how such reactions are affected by the relative amounts of the reactants; second, to examine the effect of the mole ratio of reagents on the thermal behavior of the composition and how the course of reaction is affected by isomerism; and third, to understand the nature of the matrix constituting the foam or residue and how it is modified by the amount of sulfuric acid present in the original mixture. Such a study on the isomeric nitroanilines provides a basis for more detailed studies on

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the nitroanilines themselves and for future work planned on substituted nitroanilines. On a pragmatic level, these studies may give some clues for improving uniformity and texture of the foams, for controlling density and specific surface, for changing the critical expansion temperature, and for increasing efficiency of gas retention. Finally, these studies expose a new class of pyrostats—substances that quench or restrain fires—and aphrogens—substances that expand chemically into a foam or sponge.

The first part of our work will be discussed in another paper concerned with sulfonation of nitroanilines and thermal decomposition of 4-nitro-aniline-2-sulfonic acid. The other two parts, essentially concerned with the chemistry of the foaming process itself, form the basis for this paper.

Pyrotechnic snakes,[1,2] known for a great number of years, have provided diversion and entertainment to many besides the neonatal chemist. Despite the attraction commanded by the spectacle of a large, elongated object generating from a small, ignited pellet, little if any serious effort has been made to elucidate the nature of the foam, to explore the chemistry of its creation, or to consider applications in a role more serious than trivial amusement or magic.

Over a decade ago, during comprehensive investigations on organic and inorganic foams and sponges as materials for structural, insulative, and other commercial uses, Alyea's brief description[3,4] for producing chemical "serpents" from 4-nitroacetanilide and sulfuric acid stimulated further examination of this phenomenon. This demonstration, first described by Clark in a short note,[5] has appeared in manuals on chemical magic.[6] The experiment is carried out by heating a mixture of 4-nitroacetanilide and concentrated sulfuric acid at a mole ratio of 0.47[3,4] or 1.02[5] above 200°C; the boiling black mixture erupts into an elongated, coherent black foam approaching two hundred times the original volume of the mixture if the experiment is carried out properly. Acetic acid is evolved in large amounts, and Clark believed this to be the main gaseous product.

When the mixture is heated cautiously, it is readily seen that most if not all of the acetic acid is evolved before the dramatic expansion occurs. This observation suggested that 4-nitroaniline–sulfuric acid compositions should expand equally well without evolution of obnoxious acrid fumes. The premise was verified experimentally.[7]

Exploratory investigations[7] covering numerous compounds led to the generalization that any nitroaniline bearing a nitro group ortho or para to the amino group will undergo voluminous expansion when heated with sulfuric acid. Replacement of one or more hydrogens on the ring or aminic nitrogen with other substituents does not inhibit expansion. Neither location, number, nor nature of substituent affects expansion capability if a proper heating schedule is adopted. Thus, N,N-dimethyl-4-nitroaniline, aminonitrodurene, 2,6-dibromo-(or dichloro)-4-nitroaniline, 2,4-dibromo-6-nitroaniline, 4-nitrophenylhydrazine, bis(2-nitrophenyl)urea, and other 2- and 4-nitroaniline derivatives expand with equal facility. It was further shown that a variety of naphthylamines bearing a nitro group in positions

coupled by resonance, e.g., 1,2-, 1,4-, 1,5-, and 2,6-nitronaphthylamines, as well as certain nitrated heterocyclic compounds, also expand.

Attempts to expand 3-nitroanilines were uniformly unsuccessful.[7] Even under the best of conditions expansions are less than five times the volume of the original mixtures and the coarse, brittle, sometimes reticulated chars are markedly different from the foams produced by 2- or 4-nitroanilines.

Sulfuric acid is essential in these reactions; phosphoric and other acids induce decomposition without appreciable expansion. This observation should be modified as a consequence of an observation by one of us (JAP) that 4-nitroaniline with polyphosphoric acid expands equally as well as with sulfuric acid. One of us (ACP) has also observed that nitroanilines bearing two amino groups expand voluminously when heated with phosphoric acid. Further experimental work is obviously necessary to ascertain the role of acid in these aphrogenic reactions.

The mole ratio of nitroaniline to sulfuric acid, however, is not critical; voluminous foams have been obtained from mixtures over a mole ratio range of 0.3 to 2.0 if a proper heating schedule is maintained.[7] Sulfur dioxide and water are the principal gaseous products evolved during these expansions.

Introduction of a sulfonic acid group on a nitroaniline obviates the need of sulfuric acid for expansion. These nitroanilinesulfonic acids and their onium salts[7] are particularly promising aphrogens and pyrostats. The work on 4-nitroaniline-2-sulfonic acid is the subject of a paper being prepared for publication.

Preliminary explorations suggest that the nitro group may be replaced by a nitroso group without impairing intumescence, e.g., 4-nitrosodimethylaniline heated with sulfuric acid converts smoothly into a voluminous foam having a fine texture.[7]

Some time after our extensive exploratory investigations on nitroanilines had been carried out, an interesting but short letter by Hodgson[8] confirmed our observations concerning 2- and 4-nitroaniline and 8-nitroquinoline. He also provided additional examples of aphrogenic heterocyclic compounds, i.e., nitrophenanthridine and 5-nitroisoquinoline.

Considerable impetus for continuing the study of these aphrogens came from the discovery[7] that the foams were good thermal insulators inert to chemicals, e.g., concentrated mineral acids, alkalies, organic and inorganic solvents, and oxidants. If the foam is exposed to a flame, it glows without burning and oxidizes or erodes very slowly; the radiant glow extinguishes immediately when the foam is taken away from the flame. The pyrostatic properties of 4-nitroaniline-2-sulfonic acid[7] applied to combustible materials provided further encouragement to pursue studies in this area. Recently, Parker and his group[9] have made the first successful intumescent coatings from 4-nitroanilinium bisulfate and demonstrated their efficiency in protecting substrates against fire. It is quite clear that nitroanilinium sulfates and nitroanilinesulfonic acids are a new class of aphrogenic pyrostats.

Earlier literature dealing with reactions of nitroanilines or their deriva-

tives with sulfuric acid contains an occasional comment on decomposition of such mixtures, but no evidence exists that the voluminous expansion with 4-nitroacetanilide first reported by Clark[5] and effectively publicized by Alyea[3,4] had been observed before. Boyle[10] obtained only charred products from attempted sulfonation of 4-nitroacetanilide with sulfuric acid. On the other hand, Skrowaczewska[11] baked equimolar mixtures of 2- and 4-nitroanilines and sulfuric acid at 164°C to obtain corresponding sulfonic acids without encountering decomposition or intumescence. Ammonium 2-amino-5-nitrobenzenesulfonate,[12] 2-dimethylamino-5-nitro-benzenesulfonic acid,[13] and 5-dimethylamino-2-nitrobenzenesulfonic acid[13] are reported to decompose without melting. Since each of these compounds expands over one hundred times its original volume on heating,[7] it is reasonable to infer that the decompositions were observed in a capillary tube where their spectacular expansion would be overlooked; hence the phenomenon was not reported and remained unknown.

EXPERIMENTAL

The three isomeric nitroanilines, obtained from Aldrich Chemical Co. or Sherwin-Williams, were used as received. Bromimetric analysis and melting points were in good agreement with expected values.

Due to their rapid sorption of moisture, elemental analysis[14] of the residues was carried out on material dried to a constant weight at 110°C and handled in a dry nitrogen atmosphere.

Thermogravimetric analyses were obtained on 5- to 12-mg samples in both air and helium with the du Pont instrument.[15]

Preparation of Nitroaniline–Sulfuric Acid Compositions

The requisite amount of concentrated sulfuric acid (96%; d. 1.84) was added in about 5 min to the stirred, powdered nitroaniline; maximum exotherm, reached in compositions containing most sulfuric acid, was less than 85°C. All mixtures gave a faint momentary odor of nitrobenzene. The pastes soon converted into powders, except for 2-nitroaniline-sulfuric acid, at a mole ratio of 0.52. Those compositions having a nitroaniline–sulfuric acid ratio of 0.52 and 0.67 were heated at 105°C for 5 min, and the resultant brown or yellow slurries (o-nitroaniline) or solution cooled while being stirred to obtain a uniform paste or powder. Further grinding in a mortar ensured thorough mixing. Bromine equivalence and acidity of the dried samples agreed with the calculated values. TGA of all mixtures were obtained: those at mole ratio of 0.50, 1.00, and 2.00 are given in Figure 1.

Thermal Expansion of Compositions

The required quantity of nitroaniline–sulfuric acid mixture was heated in a small beaker (50-ml size for 10-g runs; 100 ml for 40 g) at temperatures in the range 170° to 210°C while stirring the contents with a thermometer. Temperatures could be controlled within 3°C until incipient exothermal
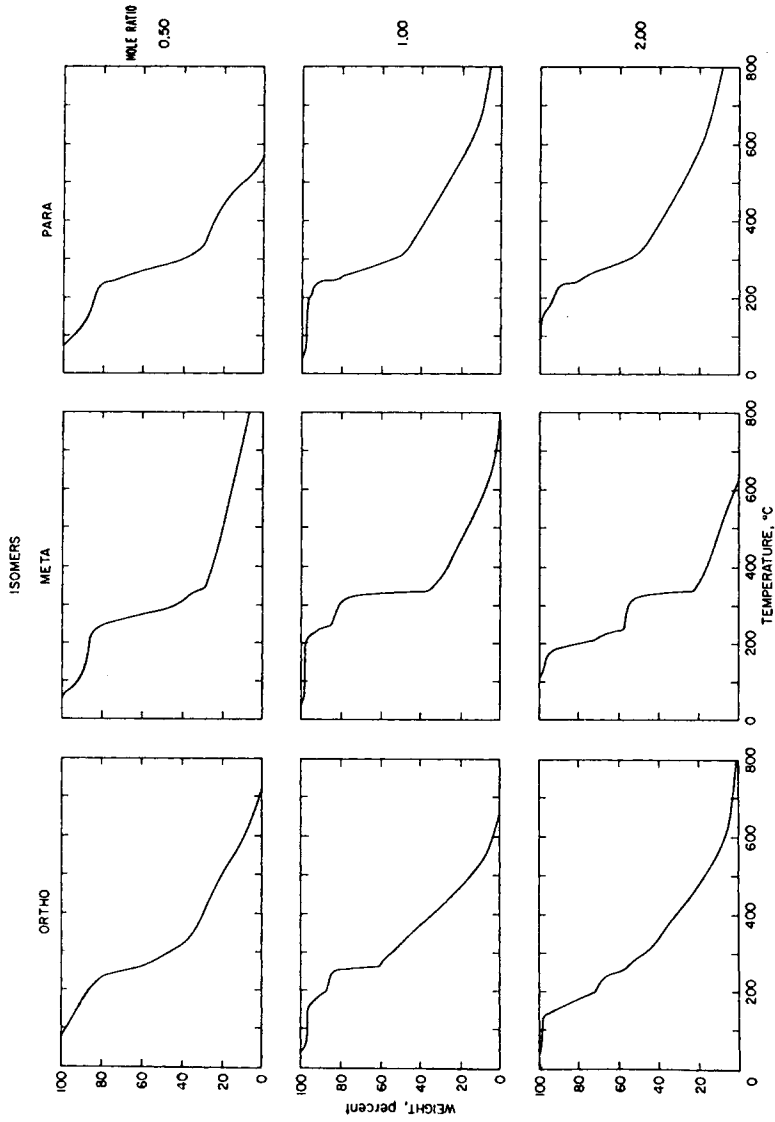
Fig. 1. TGA of nitroaniline–sulfuric acid compositions. Heating rate, 6°C/min in helium.

TABLE I
Effect of Mole Ratio and Sample Size on Yield of Residue
from Nitroaniline–Sulfuric Acid Compositions

Mole ratio aniline/ acid	Sample size, g	Residue					
		ortho		meta		para	
		%	av. %	%	av. %	%	av. %
0.52	5.0	48	55	51	50	67	59
	10.0	53		48		60	
	20.0	60		54		55	
	40.0	59		51		56	
0.67	5.0	56	60	55	48	56	58
	10.0	53		46		57	
	20.0	63		47		64	
	40.0	68		47		56	
1.03	5.0	58	56	45	42	61	55
	10.0	51		42		54	
	20.0	55		41		54	
	40.0	59		38		53	
1.55	5.0	54	48	48	45	48	49
	10.0	46		44		49	
	20.0	47		44		48	
	40.0	46		42		52	
1.98	5.0	52	47	38	42	48	49
	10.0	46		55		50	
	20.0	46		37		51	
	40.0	44		44		44	

expansion occurred. In general, we tried to induce expansion in about 15 min by raising the temperature to about 210°C. When eruption was imminent, manifest by a rapidly rising temperature and enhanced ebullition, the liquid or paste was stirred vigorously but briefly, removed from the source of heat, and the thermometer withdrawn immediately before eruption at about 230°C. The thermometer was used to steady the rising column of foam. These moderate conditions ensured smooth expansion into a coherent pillar of foam, showing some spalling at the end of the expansion and a maximum exothermal temperature of about 260°C.

Expansion can be delayed for about 1 hr by heating at 180° to 190°C. Such prolonged heating creates problems owing to conversion of nitroaniline mixtures at mole ratios less than 1 into viscous tars, gels, or rubbers difficult to stir. On the other hand, heating rapidly past incipient expansion temperatures leads to a violent eruption in less than 5 min and ejection of fragments troublesome to collect. Exothermal temperatures exceed 280°C. Under such conditions, uniform temperatures cannot be maintained, reaction is incomplete (particularly noticeable with compositions of high sulfuric acid content), and mechanical loss of material is high.

The foam obtained was weighed, and the yield was calculated after correcting for volatiles (mainly water) lost at 110°C. Yields are given in

TABLE II
Yield of Residue from Nitroaniline–Sulfuric Acid Mixtures.
Comparison with Yields from TGA

Isomer	Mole ratio aniline/acid	Residue, av. %	Yields from TGA, %		
			250°C	300°C	350°C
Ortho	0.52	55	57	49	31
	0.67	60	70	52	40
	1.03	56	68	46	39
	1.55	48	65	45	38
	1.98	47	60	44	37
Meta	0.52	50	48	31	20
	0.67	48	68	38	31
	1.03	42	82	77	29
	1.55	45	67	65	23
	1.98	42	60	59	24
Para	0.52	59	51	35	30
	0.67	58	66	43	37
	1.03	55	72	48	41
	1.55	49	66	48	42
	1.98	49	70	56	44

Table I, and these average yields are compared with those from TGA at various temperatures in Table II. The combined bodies of foam from a given mole ratio of reactants were ground in a mortar. Foams from 2- and 4-nitroaniline converted into voluminous, impalpable dusts; that from 3-nitroaniline gave a fine granular, easily-flowing powder of high bulk density.

Extraction of Residues

The powdered black foams or reaction residues were extracted consecutively with 1N sodium hydroxide, when possible, and 2N hydrochloric acid followed by water wash after each extraction. The extracts and their washings were analyzed for ionic sulfate by precipitation with barium chloride. After removing excess barium with sodium carbonate, the heated yellow filtrates were acidified and brominated. The precipitated di- or tribromonitroaniline (identified by melting point) was recovered, and the final filtrate was analyzed for ionic sulfate generated from the soluble sulfonic acids. The results are given in Tables III and IV. Material lost as volatiles when the residue and extracted residue were heated to 150°C is given in Table III.

The yield in Table IV is the amount of product recovered after final extraction of the virgin residue with hydrochloric acid, corrected for moisture sorbed. The average number of sulfonic acid groups associated with the soluble nitroanilinesulfonic acids is given in column 7 of Table IV.

Although slurries from 3-nitroaniline residues filtered easily and could be washed thoroughly, the alkaline slurries from 2- and 4-nitroaniline residues

TABLE III
Results from Extraction of Residues

Isomer	Mole ratio[a]	Virgin residue, g	Yield after extraction, g		Extract	Analysis of extract, g			Volatiles,[a] wt %		
			NaOH	HCl		$BaSO_4$ $(SO_4{}^{2-})$	Bromo-nitro-aniline	$BaSO_4$ $(-SO_3H)$	Virgin	Extd NaOH	Extd HCl
Ortho	0.52	25.0	16.4	13.0	NaOH[c]	13.77[d]	0.72	1.17	14	—	17
	1.03	25.0	20.2	17.4		5.72[d]	0.77	1.10	11	—	12
	1.98	20.0	17.6	15.0		3.10[d]	0.90	1.05	10	—	8
Meta	0.52	25.0	18.6	16.2	NaOH[c]	15.75	present	—	9	18	15
	1.03	25.0	25.1	23.9		present	present	—	13	15	16
	1.98	25.0	23.9	22.4		present	present	—	12	13	11
Para	0.52	5.00	—	3.48	HCl	3.17	0.05	0.02	13	—	10
	1.03	5.00	—	4.90		0.75	0.02	0.02	13	—	15
	1.98	5.00	—	4.96		0.24	0.09	0.04	12	—	10

[a] Nitroaniline:sulfuric acid ratio of reactants.
[b] Volatiles lost at 150°C. From TGA.
[c] Yellow extracts with hydrochloric acid gave no precipitate with barium chloride or bromine.
[d] Black precipitates.

TABLE IV
Relative Amounts of Products Extracted from Residues

| Isomer | Mole ratio[a] | Yield,[b] | Analysis of extract,[c] mmole/g | | | Sulfonic: Nitro-aniline ratio[d] |
			$BaSO_4$ ($SO_4{}^{2-}$)	Bromo-nitro-aniline	$BaSO_4$ ($-SO_3H$)	
Ortho	0.52	50	2.75	0.11	0.23	2.1
	1.03	69	1.11	0.12	0.21	1.8
	1.98	77	0.74	0.17	0.25	1.5
Meta	0.52	61	2.98	—	—	—
	1.03	93	—	—	—	—
	1.98	91	—	—	—	—
Para	0.52	72	3.14	0.039	0.020	0.5
	1.03	96	0.74	0.016	0.020	1.3
	1.98	100	0.23	0.069	0.039	0.6

[a] Nitroaniline : sulfuric acid ratio of reactants.
[b] After extraction with HCl; based on anhydrous residue and product.
[c] Based on anhydrous virgin residue.
[d] Mole sulfonic groups : nitroaniline (column 6 : column 5).

were thick grease-like pastes difficult to filter or centrifuge. The black alkaline filtrates from 2-nitroaniline residues contained small amounts of black colloidal material that coprecipitated with barium sulfate. Since the alkali-insoluble paste could not be washed well, it was not analyzed but suspended in dilute hydrochloric acid and filtered. Washing with dilute acid was carried out easily, but after two water washes the material peptized and would filter no longer.

Because the alkaline paste from 4-nitroaniline residue would not filter or centrifuge, the grease was acidified with hydrochloric acid and filtered. As with the residue from 2-nitroaniline, since thorough washing with water was not possible, washing was carried out with dilute hydrochloric acid.
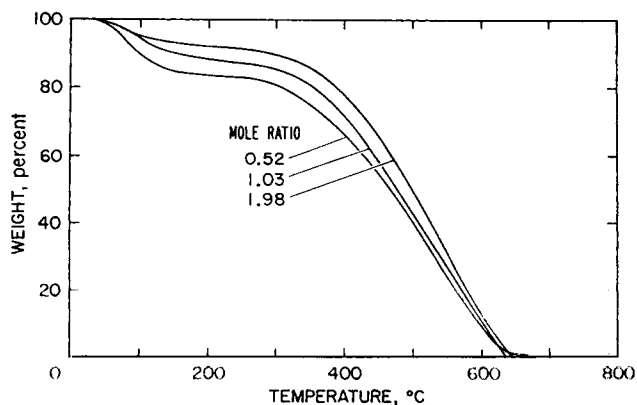

Fig. 2. TGA of expanded 2-nitroaniline–sulfuric acid mixtures. Heating rate, 6°C/min in air.

TABLE V

Composition of Extracted Residues from Expanded Mixtures of Nitroaniline–Sulfuric Acid

Mole ratio	Extractant	Isomer	Composition of insoluble residue[a] %						
			C	H	N	S	Cl	Na[b]	O[c]
0.52	HCl	o	48.44	2.57	13.45	9.58	—	0.16[g]	25.80
	NaOH	m	53.59	1.65	17.41	4.48	none	3.55	19.32
	HCl	m	56.05	1.98	18.98	3.48	0.52	none	18.99
	HCl	p[d]	52.40	2.06	16.42	6.22	0.71	0.52[h]	21.67
1.00	HCl	p[e]	56.74	2.10	22.37	3.02	1.89	0.94[i]	12.94
1.03	HCl	o	51.41	2.31	15.91	8.09	—	1.30[j]	20.98
	NaOH	m	54.27	1.42	21.47	3.21	none	3.27	16.36
	HCl	m	58.27	1.72	24.05	2.59	0.51	none	12.86
	HCl	p	54.91	2.30	20.29	5.08	1.07	0.71[k]	15.64
1.98	HCl	o	56.42	2.55	17.49	6.57	—	0.68[l]	16.29
	NaOH	m	58.02	1.85	22.44	2.51	none	2.05	13.13
	HCl	m	58.66	1.93	25.55	2.15	0.89	none	10.82
	HCl	p[f]	59.72	2.24	21.54	2.38	1.78	none	12.34

[a] Products dried at 100°C.
[b] Where indicated from ash assumed to be sodium sulfate.
[c] By difference.
[d] Loss on drying at 110°C, 20.14%.
[e] Loss on drying residue at 110°C, 17.19%. Virgin residue: 55.98% C, 2.30% H, 22.66% N, 3.14% S; loss on drying at 110°C, 15.32%.
[f] Residue was not subjected to sodium hydroxide. Loss on drying at 110°C, 12.54%.
[g] 0.5% ash.
[h] 1.6% ash.
[i] 2.9% ash.
[j] 4.0% ash.
[k] 2.2% ash.
[l] 2.1% ash.

TABLE VI
Relative Atomic Composition of Residues from
Expanded Mixtures of Nitroaniline–Sulfuric Acid

Mole ratio	Extrac-tant	Iso-mer	Relative atomic proportion (C = 6.00)					
			H	N	S	Cl	Na	O
0.52	HCl	*o*	3.83	1.43	0.45	—	0.10	2.40
	NaOH	*m*	2.20	1.67	0.19	—	0.21	1.62
	HCl	*m*	2.54	1.74	0.14	0.019	none	1.53
	HCl	*p*	2.84	1.61	0.27	0.021	0.032	1.87
1.00	None	*p*	2.95	1.82	0.13	none	none	1.29
	HCl	*p*	2.67	2.01	0.12	0.067 .	0.052	1.03
	a	*p*	3.00	1.78	0.14	none	none	1.04
	NaOH[b]	*p*	3.40	1.88	0.21	none	0.24	1.70
	HCl[b]	*p*	3.60	1.83	0.19	0.048	—	1.72
1.03	HCl	*o*	3.25	1.60	0.36	—	0.080	1.67
	NaOH	*m*	1.88	2.04	0.13	none	0.19	1.35
	HCl	*m*	2.13	2.13	0.10	0.018	none	1.00
	HCl	*p*	3.02	1.90	0.21	0.040	0.041	1.29
1.98	HCl	*o*	3.27	1.60	0.26	—	0.038	1.31
	NaOH	*m*	2.30	2.00	0.10	none	0.11	1.01
	HCl	*m*	2.38	2.26	0.083	0.031	none	0.84
	HCl	*p*	2.70	1.86	0.091	0.060	—	0.93

a From results given by Parker et al.[9]
b Poshkus, unpublished work at Armstrong Cork Co.[7]

The alkaline slurries gave off ammoniacal fumes—particularly strong from residues of compositions at low mole ratios of nitroaniline:sulfuric acid and barely perceptible by odor at a mole ratio of 2. The presence of alkaline vapors was readily demonstrated with pH paper.

The TGA profiles of residues from 2-, 3-, and 4-nitroanilines are virtually identical; therefore, curves only for 2-nitroaniline residues are given in Figures 2 and 3.
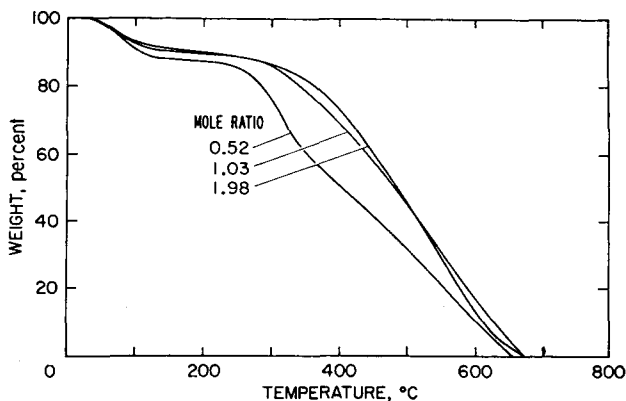

Fig. 3. TGA of expanded 2-nitroaniline–sulfuric acid mixtures after extraction with NaOH and HCl. Heating rate, 6°C/min in air.

Compositions of the extracted residues are given in Table V, and the percentages converted into relative atomic values are given in Table VI. The data are based on anhydrous products. Sodium is calculated on the assumption that the ash, given in the footnote of Table V, is sodium sulfate.

RESULTS AND DISCUSSIONS

The yield of residue or foam is unaffected by duration or rate of heating at temperatures below incipient decomposition, as shown by subjecting mixtures of nitroaniline–sulfuric acid to 170° to 200°C for 5 to 60 min before expanding them.

Within experimental error, neither sample size nor mole ratio of reactants affected the yield (Table I). This result is consistent with earlier observations on 4-nitroacetanilide[7] and with data reported by Parker and his co-workers[9] if due cognizance is given to their expanded percentile scale and to experimental error inherent in the yield.

The thermograms (Figs. 1 to 3), however, show that duration and intensity of heating affect the yield (Table II) at temperatures above 300°C. The variability in yield (Table I) is a consequence of an uncontrollable exotherm that exceeds 260°C, variable access to air, and variable heat dissipation—factors that were not controlled. Maximum exotherm was higher and heat dissipation slower for the dense residues from 3-nitroaniline than for the foams from its isomers. Chars from 3-nitroaniline remained hot for several minutes, whereas the foams from its isomers were cool in a matter of seconds. In several instances, when the coarse char from 3-nitroaniline was removed from the warm beaker and crushed, the char heated up spontaneously to over 150°C, presumably on contact with air. This effect was never observed with foams from 2- and 4-nitroanilines.

Neither texture nor volume is affected by mole ratio of reactants, but both qualities depend markedly on heating schedules. Long, uniform heating at temperatures close to incipient expansion ensures greater volume and more uniform texture. Under such conditions, even 3-nitroanilines may be expanded almost as much as five times the volume of the reactants.

Thermogravimetric analysis of all compositions and their expansion residues was carried out in air and in helium. The effect of mole ratio and isomerism can be judged from Figure 1. In air, the residue disappears at about 600°C.; in an inert atmosphere, the residue is considerably more stable. A heating rate of 3°C/min avoids anomalous tracing during the violent aphrogenic event often observed when the heating rate exceeds 6°C/min.

Nitroaniline–sulfuric acid decomposition consists of three stages (Fig. 1). The first, or preexpansion, stage is the interval up to about 230°C. Water is the major gaseous constituent, with some nitroaniline subliming at higher mole ratios; sulfur dioxide is absent (iodine test). Dehydration and sulfonation are the main chemical processes; some deamination also takes place. The second, or aphrogenic (intumescent), stage begins at about 230°C for

4-nitroaniline, at 250°C for 2-nitroaniline, and at 300°C for 3-nitroaniline, and is over within a 50° interval when the heating rate is 6°/min. Sulfur dioxide and water are major gaseous products; nitroaniline fumes are detected at higher mole ratios, and evidence for carbon dioxide is being reexamined. The third stage, in air, represents oxidative decomposition of the residue (the primary product of the exothermal reaction) and dissociation of variable amounts of ammonium salts present in the residue.

The thermal behavior of residues from all three isomers at a given mole ratio of nitroaniline to sulfuric acid is virtually identical; hence, only thermograms of residues from 2-nitroaniline are shown here (Figs. 2 and 3). Virgin residues from compositions at mole ratios of 1 and 2 are similar and only slightly different from that at a mole ratio of 0.5 (Fig. 2). Since the latter contains appreciable quantities of ammonium salts, the difference may reflect loss of ammonia by dissociation. After the residues have been washed consecutively with dilute sodium hydroxide and hydrochloric acid,

TABLE VII
Elements Accounted

Mole ratio	Ortho, %			Para, %		
	C	N	S[a]	C	N	S[a]
0.52	60	43	41	100	81	46
1.03	60	51	40	94	89	30
1.98	55	45	45	77	70	18

[a] Includes soluble sulfate and sulfonic acids.

the thermograms differ only in the amount of moisture sorbed. The sorptive capacity increases with increasing amounts of sulfuric acid in the initial composition (Fig. 3). This trend toward higher sorptive capacity with increasing sulfur content, however, is not observed with residues from 3- and 4-nitroaniline where sorption of moisture is constant at about 13% (Table III).

All expansion residues contain ammonium salts, with the greatest quantity present in residues from compositions having the most sulfuric acid. Loss of ammonium sulfate, ammonium nitroaniline sulfonate, and ammonium ions from the sulfonated residue accounts adequately for the yield of final material from 3- and 4-nitroaniline (Table IV). Ammonium salts alone cannot be the source of low yields from 2-nitroaniline after washing; acidic water-soluble organic components that give no precipitate with barium chloride or bromine must be present. This interpretation is consistent with the results given in Table VII, where considerable losses of carbonaceous products are evident. Additional support is found in the observation that filtrates from the brominations (excess bromine removed with sulfur dioxide) and hydrochloric acid washings sometimes are faintly yellow. Only chromophoric organic compounds soluble in water can produce this result.

The sulfate ions calculated as barium sulfate (Table III, column 7, and Table IV, column 4) are a consequence not only of unreacted sulfuric acid and that neutralized by ammonia, but also sulfate liberated in the decomposition of intermediate sulfonic acids[7] produced during the preexpansion stage.   With the exception of 2-nitroaniline, organic material was shown to be absent in the barium sulfate since the precipitate did not blacken on ignition.   The black precipitates obtained from 2-nitroaniline residues are mainly barium sulfate; the black colloidal particles, probably sulfonates, are estimated at about 5%.

Nitroanilinesulfonic acids bearing sulfonic acid groups ortho or para to amino groups bromodesulfonate readily.[16] Bromination of such soluble nitroanilinesulfonic acids will give sulfate ions and corresponding bromoanilines.   The mole ratio of sulfate to the bromonitroaniline indicates the extent of sulfonation.   Thus, the residue from 2-nitroaniline at a mole ratio of 0.5 contains 2-nitroaniline-4,6-disulfonic acid; at higher mole ratios, monosulfonic acids are present (Table IV).

When the residues from 4-nitroaniline are examined, an anomaly appears.   A sulfonic acid ratio greater than 1.3 is expected for a reaction mixture at a mole ratio of 0.5.   A sulfonic acid:nitroaniline ratio of less than 1 (Table IV, column 7) indicates presence of either nitroaniline sulfones or nitroaniline.   Sulfones can be expected at high but not at low mole ratios of nitroaniline.   The small amounts of 2,6-dibromo-4-nitroaniline and barium sulfate found (Table III) reduces the credibility of the ratio reported here for 4-nitroaniline.   The data require confirmation.

The residues after final extraction with hydrochloric acid invariably contain small amounts of chlorine (Table V).   Inadequate washing can explain its presence in residues from 2- and 4-nitroaniline, which we found difficult to filter and wash, particularly since the sample left an ash (sodium sulfate) clearly demonstrating incomplete ion exchange.   This explanation is untenable because the residues from 3-nitroaniline filter and wash easily, yet even the tenth washing is slightly acidic and contains chloride.   It is most likely that retention of chloride is due to weakly basic groups, e.g., amino or heterocyclic nitrogen.

It is more illuminating to consider not the analytical data itself (Table V) but the molecular composition of the residue (Table VI).   A sodium:sulfur ratio close to unity, found for the residues from 3-nitroaniline after treatment with sodium hydroxide, strongly supports the opinion that sulfur is present as sulfonic acid groups.   The extent of sulfonation decreases in the order $o > p > m$ and diminishes with decreasing amounts of sulfuric acid in the original mixture.

The presence of sulfonic acid groups is consistent with the observation that residues from 2- and 4-nitroanilines peptize readily—a behavior expected of a linear molecule bearing sulfonic acid groups.   The failure of residues from 3-nitroaniline to peptize is readily understandable if it is recognized that 3-nitroaniline behaves as a trifunctional monomer and that the residue is highly crosslinked.   Its isomers are difunctional.

Nitroaniline contains two nitrogen atoms for every six carbons. With the exception of 3-nitroaniline at mole ratios of 1 and 2, the atomic proportion of residual nitrogen is significantly less than 2 (Table VI). This result, along with the presence of ammonium ions, demonstrates extensive deamination; the extent of deamination is greatest when the amount of sulfuric acid is high.

Deamination by sulfuric acid is by no means a novel reaction. It is the basis for nitrogen determination by the Kjeldahl method[17] where an organic nitrogenous substance is heated at about 350°C with a large excess of sulfuric acid for more than 1 hr. Sulfuric acid acts as an oxidant; sulfur dioxide and carbon dioxide are produced. Despite numerous studies directed toward nitrogen determinations by this exhaustive decomposition, definitive studies on deamination of anilines under milder conditions have not been carried out. The nature of intermediates formed are unknown, but it is reasonable to believe that these intermediates are aniline-sulfonic acids.

A nitrogen atomic proportion significantly greater than 2, found in residues from 3-nitroaniline at mole ratios of 1 and 2, requires some comment. It is obvious that despite extensive deamination, recognized by the presence of ammonium ions in the residue, amination must have occurred during or after the formation of the residue.

It is of some interest to consider the atomic ratio of nitrogen to residual oxygen after subtracting the oxygen associated with sulfonic acid groups. This ratio, about 1.5 when the mole ratio of nitroaniline is 0.5, increases to a value approaching 3 at a mole ratio of 2 for 2- and 4-nitroaniline, and of 4 for 3-nitroaniline. Thus, nitro groups participate substantially in the aphrogenic process and are probably absent in the residue.

From data given in Table II to V, it is possible to assess the fraction of elements (C, N, S) recovered. Table VII shows considerable but uniform loss of material in reactions with 2-nitroaniline. This loss, probably due to soluble material not recovered by our work-up procedure, should be compared with recoveries from 4-nitroaniline. Increased loss at a mole ratio of 2 is due mainly to volatilization of nitroaniline. The major part of sulfur is lost as sulfur dioxide during intumescence.

The exact structural nature of the insoluble residue constituting the foam is unknown. All the sulfur in the residue is present as sulfonic acid groups attached to the benzene nuclei. Secondary amino or azinium groups resulting from deammoniative coupling must be present in order to account for ammonium ions and a nitrogen content less than 2 per benzene nucleus. A high nitrogen-to-oxygen ratio indicates that few if any nitro groups remain. Thus, both nitro and sulfonic acid groups are involved in oxidative processes. Nitroanilines are converted easily into azo or azoxy compounds under oxidative conditions in mildly acidic media[18] without affecting the nitro group, or in basic media with mutual coupling of amino and nitro groups.[19] Rearrangement of nitroaromatics into nitrosophenols under strongly acid conditions[20] or in the presence of alkalies[21] is known.

Nitrosoanilines and aminoazobenzenes convert into phenazines under acidic conditions.[22]   In a recent paper on the mechanism by which amino-azo compounds are transformed into indulines and rosindulines, Schroeder and Lüttke[23] demonstrated that a large excess of aniline and 2 to 3 moles of hydrogen chloride gave the best yield of phenylrosinduline (maximum 45%) after about 30 min at 140°C.   From a phenomenologic standpoint, azo, azoxy, and phenazine units may arise in reactions of nitroaniline with sulfuric acid via their sulfonic acids.   It becomes more difficult to comprehend the sequence of chemical events leading to such structures against the background of reaction conditions published and their relevance to the aphrogenic process.   The difficulty in interpretation is compounded by the observation that even compounds that normally cannot sulfonate, e.g., nitroaminodurene or 2,6-dichloro-4-nitroaniline, will intumesce on heating with sulfuric acid.   Thus, it is necessary to establish unequivocally the dominant structures of the foam matrix instead of indulging in fruitless speculations.   Work in this direction is continuing.

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