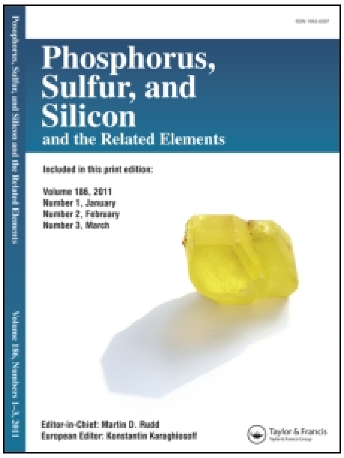

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THE DECOMPOSITION OF SODIUM N-CHLOROBENZENESULFONAMIDE (CHLORAMINE-B)

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THE DECOMPOSITION OF SODIUM N-CHLOROBENZENESULFONAMIDE (CHLORAMINE-B)

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The decomposition pressure of the hydrate of sodium N-chlorobenzenesulfonamide has been measured from 25° to 77°. Thermal analysis show that the compound undergoes two transitions accompanied by a mass loss each time. The first transition occurs at 80° to 125° and is endothermic, whereas the second one, at 188°, is exothermic. The thermal decomposition of the chloramine salt leads to the formation of sodium chloride, benzenesulfonamide, chlorobenzenesulfonamide, diphenyl sulfone, nitrogen and sulfur dioxide.

INTRODUCTION

Chloramine compounds are excellent chlorinating agents.[1–11] However, they are intrinsically unstable and storage becomes a problem particularly at elevated temperatures. With these considerations in mind, the decomposition and thermal properties of the sodium salt of N-chlorobenzenesulfonamide **1** are being studied in these laboratories. A survey of the literature failed to reveal any information about the identity of products obtained by decomposition of **1** at elevated temperatures except for a carbonaceous residue reported by Chattaway.[12]

Chattaway[12] and Zil'berg[13] studies aromatic chloramine compounds and found that **1** decomposes without melting at 180–185°C. This decomposition temperature was reproduced in these laboratories; however, we found that thermal decomposition of **1** also occurs at lower temperatures.

Mechanisms of reactions of chloramine compounds as chlorinating agents or on decomposition are not adequately understood at present. Some investigators suggest heterolytic mechanisms,[4,7–10,13] and others[14–16] suggest homolytic paths. The intrinsic instability of these materials makes adequate kinetic evaluation difficult.

PROCEDURES AND RESULTS

a) The decomposition pressure of the hydrate of **1** was measured by the static method in a manner which is described elsewhere.[17] Twenty-eight milligrams of **1** were used for this experiment. The decomposition vapor pressure data are given in Table I. The decomposition pressure as a function of temperature follows the equation $\ln P = A + (B/T) + (C/T^2)$ where the constants are $A(40 \pm 4)$, $B(-1.79 \pm 0.37)10^4$, and $C(1.75 \pm 0.46)10^6$. The constants were determined by the method of least

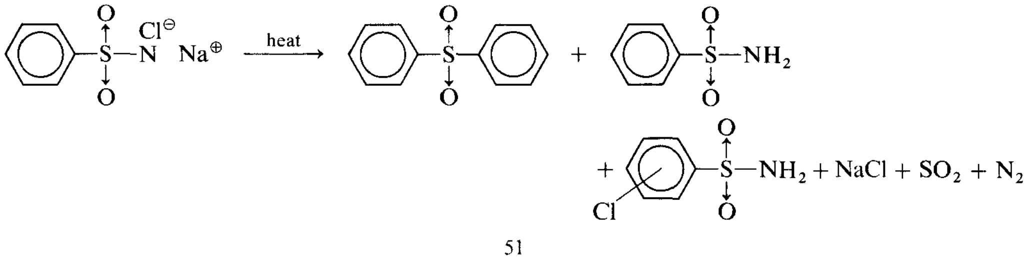

TABLE I

Vapor pressure

	Increasing temperature			Constant temperature (43.0°C)	
Temperature (°C)	Observed $P_{(torr)}$	Calculated $P_{(torr)}$	Å*H*[a] Kcal/mole	Days	$P_{(torr)}$
25.0	1.17	1.03	—	1	3.32
37.6	1.82	2.49	14.3	2	3.27
43.0	3.32	3.60	17.8	3	3.51
51.0	6.68	6.24	15.5	4	3.58
59.8	11.41	11.24	14.7	5	3.68
59.9	11.81	11.31	—	8	3.74
77.0	31.45	34.81	—	10	3.96

[a] ΔH is the enthalpy for the decomposition of the hydrate.

squares. Enthalpies for decomposition were determined graphically by plotting ln P versus T and utilizing the equation $(\mathrm{d} \ln P/\mathrm{d}T) = \Delta H/RT^2$.

b) Thermal analysis were performed on **1** using TGA and DSC. Two transitions were observed. The first, occurring over the range 80–125°, gave a 11.3% weight loss which corresponded to about 1.5 moles of water associated with **1**. The first transition was endothermic utilizing 12 kcal per mole **1**. The second transition, occurred at 188° took place violently blowing the sample out of the pan and gave irreproducible weight losses. This second transition was exothermic to the extent of 35 kcal per mole of **1**.

c) Sodium N-chlorobenzenesulfonamide was stored in a sealed glass ampul for thirty-five days at 70° after which an explosive rupture of the container occurred. An infrared spectrum of the resulting residue showed several characteristic ring vibrations (692 cm^{-1}, 710 cm^{-1}, 725 cm^{-1}, 748 cm^{-1}, 750 cm^{-1}, 762 cm^{-1} and 775 cm^{-1}) along with an ill-defined overtone spectrum at 2000–1650 cm^{-1}, suggesting a mixture of products. The mass spectrum of this sample revealed (see Table II) the coexistence of diphenyl sulfone, ring-chlorinated benzenesulfonamide, and benzenesulfonamide. An X-ray powder pattern of the residue indicated the presence of sodium chloride.

TABLE II

Mass spectral fragments for **1** stored at 70° for twenty three days

m/e	I/Io	Assignment
218	0.1	$C_6H_5SO_2C_6H_5$
193	[a]	$ClC_6H_4SO_2NH_2$
191	1	
178	[a]	$ClC_6H_4SO_2$
176	8	
157	7	$C_6H_5SO_2NH_2$
141	50	$C_6H_5SO_2$
130	[a]	C_6H_4ClO
128	1	
125	7	C_6H_5SO
114	[a]	C_6H_5Cl
112	7	
109	4	C_6H_5S
101	[a]	C_5H_5Cl
99	2	
97	11	C_5H_5S
93	22	C_6H_5O
77	100	C_6H_5

[a] Each ^{37}Cl peak was about 33% as intense as the peak due to the ^{35}Cl.

[b] Other benzene peaks.

d) A one-gram sample was placed in one end of a 4′ × 1″ pyrex tube and connected to a nitrogen tank at the same end and the other end was connected to a trap containing a dilute solution of potassium triiodide and starch indicator. The sample was heated with a bunsen burner to ignition with a constant stream of dry nitrogen acting as a carrier gas. A blue color quickly disappeared in the trap indicating that sulfur dioxide was indeed a product of the thermal decomposition.[18] The tube was then washed with acetone to remove the residue. A small amount (16 mg. av.) of carbonaceous residue was removed from this solution by filtration. The acetone solution was brought up to 100 ml and an aliquot taken for gas chromatographic analysis. This aliquot portion of the sample was evaporated to dryness on a steam bath then dissolved in methanol and diluted to 100 ml. This methanol solution was injected into the GC and the chromatogram indicated a twenty-eight mole percent content of biphenyl sulfone (two moles of **1** for each mole of diphenyl sulfone) and twenty-eight mole percent benzenesulfonamide. A separate aliquot of the acetone solution was also analyzed gravimetrically for chloride ion by treating it with distilled water and silver nitrate solution. A ninety-eight mole percent yield for the chloride ion was obtained.

A careful inspection of the mass and infrared spectra of the residue taken from the tube indicated that detectable ring chlorination did not occur.

DISCUSSION

The experimental results indicate that a portion of the N—Cl bond is hydrolyzed[19] to yield the corresponding sulfonamide. Also part of **1** undergoes disproportionation to generate diphenyl sulfone, nitrogen, sulfur dioxide and sodium chloride. This reaction may involve the elimination of the chloride ion with the simultaneous formation of an unstable nitrene radical.[20,21] The nitrene may relax to the ground state, undergo dimerization[22] and then disproportionate to the final products.

In a closed system and at elevated temperature ring chlorination is observed. This phenomenon is induced by Cl_2 or HOCl (or both). Since ring substitution was not observed for the open system, it suggests that the chlorination agent is Cl_2 generated in sufficient quantity to induce chlorination. In a separate study with **1** in KBr[23] it was found that ring chlorination did not occur until most of the hydrated water had evaporated again suggesting that $Cl_2(Cl)^+$ was the chlorinating species.

EXPERIMENTAL

Chemicals

Sodium N-chlorobenzenesulfonamide was the product of Mine Safety Appliance Corporation of Pittsburgh, Pennsylvania. This compound was used without further purification, since recrystallization from aqueous medium yielded a progressive decrease in active chlorine due to hydrolysis. Elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and **1** was found to contain 29.69% C, 3.27% H, 15.04% Cl, 13.21% S, 10.27% Na, and 5.96% N. The theoretical values for $C_6H_5SO_2NClNa \cdot 1.5H_2O$ are 31.2% C, 3.48% H, 15.38% Cl, 13.9% S, 10.0% Na and 6.10% N. All other reagents were of the best quality commercially available.

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