

## THERMOCHEMICAL STUDIES OF SYM-DICHLOROBIS (2,4,6-TRICHLOROPHENYL) UREA

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### ABSTRACT

Thermal decomposition of sym-dichlorobis (2,4,6-trichlorophenyl) urea occurs by two steps: the first at 150–184°C accompanied by a 26% weight loss and  $+ (16.6 \pm 0.7) \text{ kcal mole}^{-1}$  and the second by a 40% weight loss and  $- (17.4 \pm 1.0) \text{ kcal mole}^{-1}$ . The decomposition pressure follows the equation  $\ln p = A + B/T + C/T^2$  where  $A = 149.89$ ,  $B = 9.45 \cdot 10$  [4] and  $C = 1.48 \cdot 10$  [7]. The decomposition products are 2,4,6-trichlorophenyl isocyanate, 2,4,6-trichloroaniline, chlorine, 1,2,3,5-tetrachlorobenzene, 2,2',4,4',6,6'-hexachlorobiphenyl, 2,2',4,4'-tetrachlorobiphenyl, 2,2',4,4',6-pentachlorobiphenyl and ammonium chloride.

### INTRODUCTION

Chloramine compounds have long been used as chlorinating agents [1–3]. The N–Cl bond is generally unstable and particularly so at elevated temperatures. Their thermal instabilities have been reported [4] but a survey of the literature failed to reveal the identity of the decomposition products except for a carbonaceous residue. With these thoughts in mind, the decomposition and thermal properties of sym-dichlorobis (2,4,6-trichlorophenyl) urea, I, are being investigated in these laboratories.

Chloramine compounds' reaction mechanisms of thermal decomposition and as chlorinating agents are not adequately understood at present. Their intrinsic instability makes suitable kinetic evaluation difficult; however, some investigators suggest heterolytic mechanisms [5–7] and others recommend homolytic paths [8–10]. This investigation involves the thermal properties of I and the identification of its

decomposition products without attempting the difficult task of a detailed kinetic investigation.

## EXPERIMENTAL

### *Materials*

Sym-dichlorobis (2,4,6-trichlorophenyl) urea was supplied by Edgewood Arsenal, Edgewood, Md. It was purified by a three-fold recrystallization using warm glacial acetic acid as a solvent and then adding distilled water as a non-solvent. All reagents used were the best commercially available.

### *Infrared spectrum*

A KBr disc was prepared with the recrystallized chloramine and a spectrum was obtained using a Beckman IR-20A-X spectrophotometer. The absorption bands are as follows in  $\text{cm}^{-1}$  (s = strong, m = medium, w = weak, and sh = shoulder): 3800–3500 m, 3260 m, 3055 w, 1700 s, 1665 shs, 1635 s, 1625 shm, 1540 s, 1520 s, 1480 s, 1430 m, 1405 m, 1370 shm, 1355 m, 1290 shm, 1260 s, 1205 s, 1132 m, 1120 m, 1058 w, 1000 w, 913 w, 880 shw, 840 s, 828 m, 800 s, 788 shs, 750 w, 690 w, 660 w, 585 w, 550 shw, and 538 w.

### *DSC and TG*

DSC analyses were performed on a Perkin-Elmer Model DSC-1B differential scanning calorimeter. Six samples ranging in mass from 2.6 to 3.8 mg were prepared in aluminum sample holders and run with a programmed temperature increase of  $10 \text{ deg min}^{-1}$ . Enthalpies for observed transitions were calculated by comparison with the heat of fusion for a standard indium sample supplied by Perkin-Elmer of Norwalk, Connecticut.

TGA analyses were performed on a Cahn RG electrobalance with a Fisher TGA accessory. Approximately 10 mg of sample was placed in a platinum sample holder and then heated in air with a constant temperature increase of  $10^\circ\text{C min}^{-1}$ .

TG and DSC showed two transitions occurring on heating the subject compound. The first transition took place over the temperature range of  $154\text{--}188^\circ\text{C}$  accompanied by a 26% weight loss.  $\Delta H$  for this transition was  $+(16.6 \pm 0.7) \text{ kcal mole}^{-1}$ . The second transition appeared at  $205\text{--}212^\circ\text{C}$  with a 40% decrease in mass and  $\Delta H$  was found to be  $-17.4 \pm 1.0 \text{ kcal mole}^{-1}$ .

### *Decomposition pressure*

Decomposition pressures were measured by the static method in a similar manner to that described elsewhere [11] except the temperature range was  $90\text{--}150^\circ\text{C}$  and a

26 mg sample of I was placed in the sample compartment. A least squares treatment of the data showed that the decomposition pressure followed the equation  $\ln p = A + B/T + C/T^2$  where,  $A = -149.89$ ,  $B = 9.45 \times 10^4$  and  $C = 1.48 \times 10^7$ . The data points were 90.2°C ( $0.43 \pm 0.06$  Torr), 105.1°C ( $1.36 \pm 0.06$  Torr), 120.2°C ( $4.57 \pm 0.06$  Torr), 135.5°C ( $8.30 \pm 0.09$  Torr) and 150.2°C ( $12.49 \pm 0.13$  Torr).

#### *Elimination of chlorine*

A small sample of I was placed in the solid injection port of a mass spectrograph (Model RMU-6 Hitachi—Perkin-Elmer mass spectrometer). The temperature was programmed to increase and mass spectra were taken at several temperatures (see Table I). The intensities of the  $m/e$  peak at 35 were compared with that of  $m/e$  32.

Subsequent to the above experiment, a 1 g sample of I was placed in a  $25 \times 150$  mm test tube. A piece of bent glass tubing fitted in a one hole neoprene stopper was inserted into the test tube. The entire assembly was positioned such that the glass tube projected into  $\text{CCl}_4$  with a solution of 0.2 F KI above it (both being contained in a second flask). The samples were then thermally decomposed by heating with a bunsen burner. The chlorine liberated from the sample was then determined iodometrically using 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The average chlorine yield was 13.9%.

#### *Analysis of the decomposition residue*

0.5 g of I were placed in a 100 ml standard taper round bottomed flask and then a water cooled condenser was fitted to the flask before being clamped in the upright position. Approximately one-half of the flask was submerged in a silicon oil bath. The silicon oil bath was heated until the sample decomposition was completed. The decomposition started to occur with a bath temperature of 210°C and appeared to terminate at 220°C. The sample and flask were removed from the bath and allowed to cool to room temperature. The condenser was thoroughly rinsed with  $\text{CHCl}_3$  into the flask and the entire mixture was gravity filtered.

TABLE I

Temperature (°C)	$I^{35}$ (mm)	$I^{32}$ (mm)	$I^{35}/I^{32}$
130	1.5	85	0.018
140	2	87	0.023
150	2	88	0.023
160	4	86	0.047
170	4	83	0.048
180	9	83	0.108
190	12	85	0.142
200	16	73	0.219

TABLE 2  
Mass spectral data <sup>a</sup>

Compound	<i>m/e</i> (Relative intensities)
2,4,6-Trichloroaniline	201 (2), 200 (1), 199 (26), 198 (4), 197 (96), 196 (4), 195 (100), 163 (1), 162 (3), 161 (4), 160 (4), 159 (7), 150 (1), 149 (4), 135 (3), 134 (2), 133 (5), 132 (2), 126 (4), 125 (3), 124 (18), 110 (2), 100 (1), 99 (3), 98 (7), 97 (8)
2,4,6-Trichlorophenyl isocyanate	221 (1), 205 (2), 195 (1), 180 (2), 179 (1), 166 (1), 165 (13), 150 (1), 149 (3), 138 (1), 137 (1), 125 (2), 124 (2), 123 (5), 122 (10), 110 (34), 111 (3), 108 (12), 96 (9), 95 (24), 94 (7), 93 (4), 85 (5), 84 (33), 83 (21), 82 (9), 81 (6), 72 (3), 71 (26), 70 (100)
1,2,3,5-Tetrachlorobenzene	220 (7), 218 (43), 216 (100), 214 (76), 183 (3), 181 (15), 179 (16), 149 (6), 146 (1), 145 (5), 144 (3), 143 (9), 109 (11), 108 (15)
2,2',4,4'-Tetrachlorobiphenyl	296 (12), 294 (36), 292 (100), 290 (71), 259 (6), 257 (24), 255 (18), 224 (7), 223 (10), 222 (54), 220 (74), 210 (4), 197 (2), 195 (3), 187 (3), 186 (4), 185 (7), 184 (10), 171 (1), 160 (3), 159 (3), 158 (4), 151 (3), 150 (18), 149 (31), 131 (2), 129 (3), 127 (5), 112 (2), 111 (11), 110 (17), 101 (2)
2,2',4,4',6-Pentachlorobiphenyl	328 (10), 326 (18), 324 (14), 296 (7), 294 (39), 293 (13), 292 (84), 291 (10), 290 (60), 281 (6), 256 (12), 254 (12), 224 (5), 223 (12), 222 (29), 221 (12), 220 (45), 211 (5), 210 (18), 207 (13), 187 (5), 185 (9), 184 (15), 164 (5), 161 (5), 151 (5), 150 (18), 149 (86), 135 (9), 134 (6), 133 (9), 132 (5), 131 (7), 129 (7), 123 (8), 122 (6), 121 (8), 119 (6), 117 (5), 111 (11), 110 (16), 109 (10), 108 (6), 107 (6), 105 (11), 104 (15) <sup>b</sup>
2,2',4,4',6,6'-Hexachlorobiphenyl	366 (7), 365 (3), 364 (27), 363 (9), 362 (87), 360 (100), 359 (6), 358 (40), 327 (6), 325 (18), 324 (2), 323 (4), 294 (4), 293 (5), 292 (32), 290 (57), 289 (6), 288 (35), 281 (3), 255 (4), 254 (5), 253 (4), 252 (5), 222 (3), 221 (4), 220 (14), 219 (4), 218 (19), 210 (11), 207 (4), 206 (3), 205 (5), 197 (3), 193 (2), 191 (2), 184 (3), 183 (4), 182 (7), 181 (7), 180 (6), 163 (5), 162 (6), 150 (4), 149 (36), 148 (4), 147 (5), 146 (10), 145 (22), 144 (13), 128 (7), 127 (9), 126 (8), 110 (9), 109 (12)

<sup>a</sup> All common benzinoid peaks were omitted.

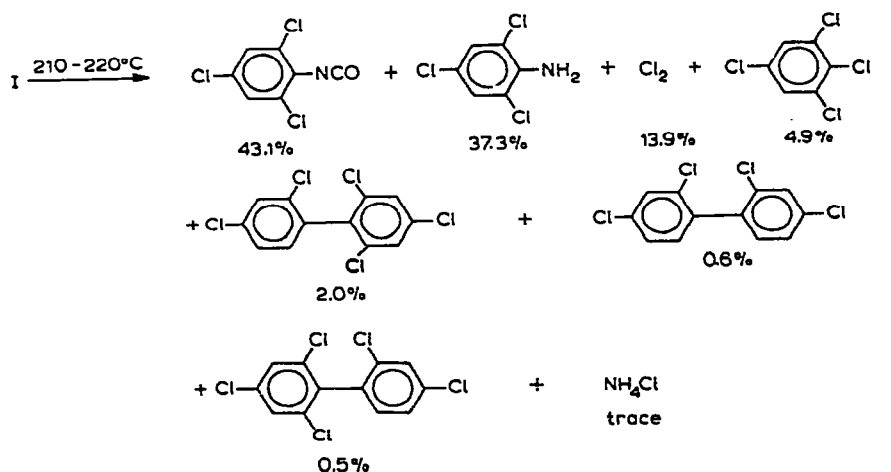
<sup>b</sup> Relative to *m/e*=44.

(1) The chloroform soluble portion was subsequently diluted to a known volume. An aliquot of this solution was found to contain a mass equal to  $(40.3 \pm 1.0)\%$  of the original sample by weight. Mass spectra of the components of this solution were obtained by injecting about 50 ng of the sample into a Finnigan 4021 GC/MS/DS mass spectrometer. The GC was equipped with a 30 m capillary column. Helium was used as a carrier gas with a flow rate of  $0.5 \text{ ml min}^{-1}$  under a pressure of 9 p.s.i. The column was programmed for a  $10 \text{ deg min}^{-1}$  temperature increase over the range  $50\text{--}235^\circ\text{C}$ . The solution was found to contain 88 relative percent 2,4,6-trichloroaniline (See Table 2) and 12 relative percent 1,2,3,5-tetrachlorobenzene.

(2) The chloroform insoluble portion of the residue represented 53.5% of the original sample. From among several common solvents tested this residue was found to be soluble in ethylenediamine. After dissolving a known weight of the chloroform insoluble residue to a known volume in ethylenediamine, it was analyzed in the same GC/mass spectrometer. The results were: 82.1 relative percent 2,4,6-trichlorophenyl isocyanate, 3.4 relative percent 2,4,6-trichloroaniline, 1.2 relative percent 2,2',4,4'-tetrachlorobiphenyl, 9.8 relative percent 2,2',4,4',6-pentachlorobiphenyl and 3.8 relative percent 2,2',4,4',6,6'-hexachlorobiphenyl (see Table 2). The chloroform insoluble residue was also extracted with distilled  $\text{H}_2\text{O}$  and the aqueous extract was then tested for  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions using the standard qualitative test. The tests were positive indicating that a small amount of each ion was present.

## DISCUSSION

The thermal decomposition of I is represented by the reaction



The IR spectrum of the starting material indicates the possible presence of a small amount of water with a broad absorption band at  $3800\text{--}3500 \text{ cm}^{-1}$  [12] and a shoulder at  $1625 \text{ cm}^{-1}$  [13,14]. The occurrence of bands at  $3260 \text{ cm}^{-1}$ ,  $1665 \text{ cm}^{-1}$  [15–17],  $1540 \text{ cm}^{-1}$  [18,19],  $690 \text{ cm}^{-1}$  [20] and  $660 \text{ cm}^{-1}$  [21] indicate that complete chlorination of the urea nitrogen was not accomplished during the original synthesis. As a final observation the weak bands at  $880$  and  $828 \text{ cm}^{-1}$  suggest that incomplete

ring chlorination also exists partially justifying the formation of 2,2',4,4'-tetrachlorobiphenyl and 2,2',4,4',6-pentachlorobiphenyl. However, aromatic dehalogenation may also lead to the formation of these products as was observed by Smalley and Suschitzky [23] if a nitrene is involved in the decomposition reaction.

2,4,6-Trichloroaniline, 2,4,6-trichlorophenyl isocyanate, chlorine or hydrogen chloride, 2,4,6-trichloroazobenzene and ammonium chloride [23-26] are the expected products for this thermal degradation if a nitrene is produced during the initial phase of the reaction accompanied by the formation of 2,4,6-trichlorophenyl isocyanate and chlorine (or HCl). The fact that no azo compound is found among the products suggests that the nitrene is preferentially in the more stable singlet state [27]. The nitrene forms aniline by hydrogen abstraction from hydrogen chloride or water or it decomposes to produce ammonia and 1,2,3,5-tetrachlorobenzene or the biphenyl compounds.

As a final observation the hydrogen ion concentration must have remained sufficiently high during the course of the overall reaction to suppress the loss of gaseous ammonia and prevent isocyanate dimerization or trimerization.

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