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THE THERMAL DECOMPOSITION OF SYM-DICHLOROBIS (2,4,6-TRICHLOROPHENYL) UREA IN KBr

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ABSTRACT

Infrared spectra of sym-dichlorobis (2,4,6-trichlorophenyl) urea over the range 4000–250 cm^{-1} have been obtained on samples prepared in KBr discs and stored for several hours at elevated temperatures. The subject compound undergoes thermal decomposition by cleavage of the N–Cl bond and the formation of sym-2,4,6-trichlorophenyl urea with some aromatic halogenation of 2,4-dichlorophenyl groups present in the sample.

INTRODUCTION

N-Chloro compounds have long been recognized as excellent chlorinating agents [1–5] but they are inherently unstable, especially when exposed to elevated temperatures [6,7]. Little effort has been expended to thoroughly investigate the deflagration reactions of these compounds by identifying the products formed by their decomposition. To address this latter problem a few monographs have recently appeared in the literature [8–10].

In a previous report [10] sym-dichlorobis (2,4,6-trichlorophenyl) urea (I) was found to decompose upon melting to yield 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. With this information it seemed obvious that the thermal stability of I should be investigated at temperatures below the melting point. This study is an attempt to look at the behavior of I under the special condition where the decomposition vapors are partially entrapped in the host matrix, namely KBr.

EXPERIMENTAL

Sym-dichlorobis (2,4,6-trichlorophenyl) urea was supplied by Edgewood Arsenal, Edgewood, MD. It was further purified by reprecipitation from a

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TABLE 1

Infrared spectra of sym-dichlorobis (2,4,6-trichlorophenyl) urea (cm^{-1})

Nujol mull on NaCl	KBr disc			Assignment	Ref.
	Before heating	After heating at 150°C			
		24 h	92 h		
	3600–3400 w			OH stretch	11
3305 bs	3300 bs	3300 bs	3300 bs	NH stretch	12,13
3210 sh	3210 sh	3210 sh	3210 sh	NH stretch	13
3090 m	3095 m	3095 m	3095 w	CH stretch	14
		2280 m		NCO	15
1710 s	1722 s	1740 bm	1740 bw	C=O	16,17
1670 s	1686 s			C=O	16
1650 sh	1670 s	1660 s	1660 s	Amide I	13,16,18
1630 sh	1640 sh	1640 sh	1640 sh		
1560 bs	1570 s	1575 s	1575 s	C–C skeletal	13,19,20
1535 m	1550 m	1540 s	1540 s	Amide II	13
1490 s	1500 s			C–C skeletal	18
1450 bs	1450 s	1450 s	1450 s	C–C skeletal	19,21
1420 w	1430 m	1435 w	1435 w		
1385 sh	1390 m	1388 m	1386 m		
	1378 m	1374 m	1372 m		
1305 m	1320 w	1335 w	1335 w	Amide III	13
1275 m	1280 m	1276 m	1276 m	(1235)	22
1260 sh	1275 sh			(124)	23
1215 s	1225 s	1230 bm	1230 bm	(1235)	22
1180 w	1190 w	1190 w	1190 w	Amide II	13
1130 m	1140 m	1135 m	1132 w	(124)	23

1080 w	1085 w	1075 w	1073 w		
1070 w	1060 w	1055 w	1054 w		
1015 w	1027 w			(124)	23
925 w	938 w			(124)	23
910 w	920 w	920 m	920 m	(1235)	22
895 w	892 w			(124)	23
860 sh	870 sh	870 sh	870 sh	(124)	23
852 s	864 s	860 vs	860 vs	(1235)	22
836 m	838 m	836 w	836 w	(124)	23
812 s	825 s	820 s	820 s	(124)	23
795 s	805 s	800 s	800 s	(1235)	22
760 w	770 w	770 vw	770 vw?	C–Cl(124)?	
		745 w	745 w	C–Br	24
700 w	712 w	710 m	708 m	(1235)	22
	682 w	680 vw	680 vw?	(124)	23,25
		630 bm	630 bm	Amide IV	13
	588 w	590 vw		N–Cl	26,27
	562 m	566 m	562 m		
	550 m	550 sh	550 sh	ϕCCC(124)?	
		488 m	482 m	ϕCCC	28
	418 w			Lattice H_2O	29
	390 m	398 m	392 m	αCCC	28

b = Broad, sh = shoulder, s = strong, m = medium, w = weak.
(124) = C–H Deformation for 124 phenyl substitution.
(1235) = C–H Deformation for 1235 phenyl substitution.

ution in which hot reagent grade glacial acetic acid served as a solvent and tilled water was added as a non-solvent. The recrystallized compound was n stored under vacuum over anhydrous phosphoric acid for several days. A KBr disc was prepared in the usual manner with previously dehydrated tassium bromide and I. An IR spectrum was immediately obtained then KBr disc with the sample was stored in a drying oven at elevated nperatures of 115, 123 and 150°C, using a new sample for each tempera- e. The samples were removed at 24 h intervals, allowed to cool to room nperature, and IR spectra were obtained until no noticeable change could observed. The same trends were obtained for each of the three tempera- es but the results for 150°C were selected to report along with the ctrum of I in nujol (see Table 1). An IR spectrum of KBr established that re was no detectable water present.

SCUSSION

Heating I in a KBr disc produced a blackened sample indicating that the composition reaction had taken place as was reported previously [10] for s compound above its melting point. A comparison of the spectra for I in jol and KBr indicates that it remains essentially stable on being com- ssed into the KBr.

With regard to the spectrum of the sample in KBr before storing at vated temperature there are some pertinent observations that should be de: (1) There is evidence of a small amount of water in the sample as licated by the broad weak band at 3600–3400 cm^{-1} [11] and at 418 cm^{-1}]. (2) The bands at 1722, 1686 and 1670 cm^{-1} are due to the CO group of $_2Cl_2N_2CO$, Ar_2ClHN_2CO and $Ar_2H_2N_2CO$, respectively [13,16,18] erein the νCO is hypsochromatically shifted by the presence of the ctronegative chlorine on the adjacent nitrogen atom(s). (3) In comparing spectrum of I in KBr with the Aldrich spectra of 2,4-dichloroaniline [23] d 2,4,6-trichloroaniline [22], the in-plane and out-of-plane C–H deforma- ns at 1275, 1140, 1027, 938, 812, 870, 838, 825, 682, 550 cm^{-1} and rhaps 770 cm^{-1} are being attributed to 2,4-dichloro substitution of the enyl ring. Furthermore, the bands at 1280, 1225, 920, 864, 805 and 712 $^{-1}$ are associated with the 2,4,6-trichlorophenyl group.

On storing the KBr sample of I at elevated temperatures, the bands at 0–3400 and 418 cm^{-1} disappeared, indicating that the water is lost ough evaporation or consumed during the decomposition reaction. The pearance of the band at 2280 cm^{-1} and its subsequent disappearance eal the formation of some aryl isocyanate [15] as an intermediate in the erall reaction. The weakening of the band at 1722 cm^{-1}, the disappearance the band at 1686 cm^{-1} and the continued presence of the amide II band 1660 cm^{-1} show the loss of nitrogen bonded chlorine followed by the formation of diaryl urea. A decrease in the intensities of the bands at 1275, 1140, 1027, 938, 890 and 682 cm^{-1} suggests that some aromatic chlorination of the residual 2,4-dichlorophenyl group occurred. Finally, the appearance of the weak band at 745 cm^{-1} may be attributed to a limited amount of bromination of the 2,4-dichlorophenyl group, however, due to the nature of the sample distribution within the KBr matrix this reaction is quite limited in its occurrence.

In conclusion, the decomposition of I in the solid state leads to a different set of products than previously reported for the liquid phase [10]. The reaction apparently proceeds by the elimination of Cl_2 (or HCl) and the simultaneous formation of 2,4,6-trichlorophenyl isocyanate and the 2,4,6-trichlorophenyl nitrene (or the 2,4-dichlorophenyl analogues). The nitrene stabilizes itself by combining with HCl or H_2O to become the corresponding aniline. Finally, the aniline derivative and the isocyanate recombine to form sym-2,4,6-trichlorophenyl urea. In this case where evaporation of chlorine is somewhat restricted some aromatic chlorination occurred whereas the decomposition of I in the liquid phase led to almost complete loss of Cl_2 as a gas.

REFERENCES

1 A.E. Bradfield, J. Chem. Soc. (London), (1928) 351.
2 R.S. Neale and N.L. Marcus, J. Org. Chem., 32 (1967) 3273.
3 C.W. Poter and P. Wilbur, J. Am. Chem. Soc., 49 (1927) 2195.
4 V.R.S. Rao, Indian Chem. Manuf., Annu. Number 8 (1969) 118.
5 L.O. Brown and F.G. Soper, J. Chem. Soc., (1953) 3576.
6 F.D. Chattaway, J. Chem. Soc., 87 (1905) 145.
7 I.G. Zil'berg, J. Gen. Chem. U.S.S.R., 16 (1946) 2145.
8 L. Gelfand, L.L. Pytlewski and C. Owens, Spectrochim. Acta, Part A, 35 (1979) 79.
9 C. Owens, C.K. Johnston, D.L. Wilson, L. Gelfand and L.L. Pytlewski, J. Phos. Sulfur Chem., 8 (1980) 51.
10 C. Owens, L.L. Pytlewski, K. Krevitz and T. Mitchell, Thermochim. Acta, 54 (1982) 281.
11 P.J. Lucchesi and W.A. Glasson, J. Am. Chem. Soc., 78 (1956) 1347.
12 J.A. Lacher, G.G. Olson and J.D. Park, J. Am. Chem. Soc., 74 (1952) 5578.
13 C.I. Jose, Spectrochim. Acta, Part A, 25 (1969) 111.
14 J.T. Fox and A.E. Martin, J. Chem. Soc., (1939) 318.
15 N.S. Ham and J.B. Willis, Spectrochim. Acta, 16 (1960) 279.
16 R.E. Richards and H.W. Thompson, J. Chem Soc. (London), (1947) 1248.
17 S. Pinchas and D. Samuel, J. Chem. Soc. (London), (1954) 863.
18 N.B. Colthup, J. Opt. Soc. Am., 40 (1950) 397.
19 A. Depaigne-Delay and J. Lecomte, J. Phys. Radium, 7 (1946) 38.
20 D. Wiffin, J. Chem. Soc., (1956) 1350.
21 M.L. Josien and J.M. Lebas, Bull. Soc. Chim. Fr., (1956) 53.
22 C.J. Pouchert, Aldrich Library of Infrared Spectra, 2nd edn., Aldrich Chem. Co., Milwaukee, WI, Spectra No. 14,571-8.
23 C.J. Pouchert, Aldrich Library of Infrared Spectra, 2nd edn., Aldrich Chem. Co., Milwaukee, WI, Spectra No. 11,215-1.

24 F.S. Mortimer, R.B. Blodgett and F. Daniels, J. Am. Chem. Soc., 69 (1947) 822.
25 R.L. Werner, W. Kennard and D. Rayson, Aust. J. Chem., 8 (1955) 346.
26 W.G. Burns and H.J. Bernstein, J. Chem. Phys., 18 (1950) 1669.
27 G.E. Moore, J. Am. Chem. Soc., 74 (1952) 6075.
28 T. Uno, K. Machida and K. Hanai, Spectrochim. Acta, Part A, 24 (1968) 1705.
29 J. Van der Elsken and D.W. Robinson, Spectrochim. Acta, Part A, 17 (1961) 1249.