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THE THERMOLYSIS OF TRIMETHYLAMINE PHENYLCARBAMIMIDE

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Certain carbamoyl azides have been reported[1] to undergo thermolytic and photolytic Curtius rearrangements. Since amine imides derived from carboxylic acids ($RCO\overset{-}{N}\overset{+}{N}R'_3$) undergo thermolytic Curtius-Hoffman type rearrangements[2] (initiated by loss of tertiary amine), it was of interest to examine the thermolysis and photolysis of trimethylamine phenylcarbamimide (I).[3] The corresponding azide ($C_6H_5NHCON_3$) has been rearranged by photolysis in methanol[1] but thermolysis in protic[4] and aprotic[5] solvents gave unrearranged products.

We have found that the major pathway for the thermolytic decomposition of I differs markedly from that observed for the azide. When heated at 230°, I decomposed rapidly to give trimethylamine (identified as its picrate), water insoluble gases and a dark residue from which pure 1,3-diphenylurea was isolated. Mass spectrographic analysis[6] of the gaseous products revealed the presence of both CO and N_2. Although a quantitative analysis of the relative amounts of these gases was not undertaken, N_2 predominated since the $N_2^+:CO^+$ peak height ratio was 2:1.

The above observations suggest the following stoichiometry for the predominant reaction:

$$2\ \underset{\text{I}}{C_6H_5NHCO\overset{-}{N}\overset{+}{N}(CH_3)_3} \rightarrow C_6H_5NHCONHC_6H_5 + 2(CH_3)_3N + CO + N_2$$

Assuming this stoichiometry to be correct, the yield of pure diphenylurea was 50%, and the combined yield of CO and N_2 was 62%. The presence of excess

N_2 indicates other pathways, but we have been unsuccessful in isolating other products from the complex mixture remaining after isolation of diphenylurea.

Since N_2 is formed in the thermolysis reaction, it is tempting to write a mechanism involving azobisformanilide (III) as an intermidiate which could form from attack of the carbamoyl nitrene (II) on the amine imide, from nitrene dimerization or in a more complex manner without involving the nitrene.[7] Compound III could then thermally decompose to give the products.

$$\mathrm{I} \xrightarrow[-(CH_3)_3N]{} \underset{\mathrm{II}}{C_6H_5NHCO\overline{\underline{N}}} \rightarrow \underset{\mathrm{III}}{C_6H_5NHCON{=}NCONHC_6H_5} \rightarrow C_6H_5NHCONHC_6H_5 + CO + N_2$$

Azo compounds have been previously isolated[7] or implicated[8] in the decomposition of various azides, including carbamoyl azide.[9] Although the intermediacy of the carbamoyl nitrene is speculative, the evidence for the formation of the intermediate azo compound III is more compelling. The latter compound was initially prepared by Curtius and Burkhardt[3] in 1898, but its mode of thermal decomposition has apparently not been studied. We have found that on heating at its decomposition temperature (180°) it rapidly gives 1,3-diphenylurea (63%), CO, and N_2 and a mixture of unidentified products. The CO and N_2 were detected by mass spectrometry. N_2 was again found to predominate (N_2^+:CO^+ peak heights 2:1).

Since the neat thermal decomposition temperature of III is ca. 50° below that of I the detection of the azo compound under the conditions of the reaction is not possible.

Starting material was isolated, together with a minute quantity of tarry material when a 1% methanolic solution of I was photolyzed for 24 hours.

Further studies of amine carbamimides and carbamoyl azo compounds are in progress.

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