The Thermal Decomposition of Primary Aromatic Nitramines

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THE acid-catalysed rearrangement of primary aromatic nitramines has been studied in detail[1] whereas the thermal decomposition has received little attention.[2]

The thermal decomposition of primary aromatic nitramines in aromatic solvents has been found to produce biaryls, *e.g.* 4-nitrophenylnitramine in nitrobenzene gave a mixture of biaryls from which 4,4′-dinitrobiphenyl was isolated. The decomposition is accompanied by the evolution of nitrogen (identified by mass spectrometry[3]) and the formation of water. Decomposition of nitramines in octan-2-ol gives the substituted aromatic hydrocarbon, nitrogen, water, and methyl n-hexyl ketone (Table).

TABLE

Products from the decomposition of primary aromatic nitramines in octan-2-ol at 120°

Substituted phenylnitramine	Yield of nitrogen[a]	Yield of methyl n-hexyl ketone[a,b]	Substituted hydrocarbon[a] (%)	Yield of water[d] (%)
4-nitro	72·5	59	Nitrobenzene (48·5)	80
4-methyl	71·5	33	Toluene (45)	56
2,4-dinitro	67·5	30	1,3-Dinitrobenzene(21)[c]	69
2,5-dichloro	70·0	27	1,4-Dichlorobenzene (50)	100
2,4,6-trinitro	95·0	63		100
2,4,6-trimethyl	75·0	23	1,3,5-Trimethylbenzene (43)	95
2,4,6-tribromo	51·0	27	1,3,5-Tribromobenzene (11)[c]	50

[a] Yields determined by gas liquid chromatography; [b] Yields based on 1 mole of nitramine oxidises 2 moles of alcohol; [c] Yield of isolated material; [d] Yield based on 1 mole of nitramine gives 2 moles of water.

The biaryl and substituted aromatic hydrocarbon formation shows that aryl radicals are produced. A mechanism which accounts for the observed products is shown below:

$$\mathrm{ArNHNO_2 \rightleftharpoons ArN{=}N(:O){\cdot}OH}$$

$$\mathrm{ArN{=}N(:O)OH \rightarrow HO^{\cdot} +}$$

$$\mathrm{Ar\overset{+\cdot}{N}{=}\overset{-}{N}{-}O \longleftrightarrow ArN{=}N{-}O^{\cdot}}$$

(I)

$$\mathrm{ArN{=}N{-}O^{\cdot} + RH \rightarrow ArN{=}NOH + R^{\cdot}}$$

(II)

$$\mathrm{ArN{=}N{\cdot}OH \rightarrow}\ \text{Products due to ionic coupling}$$

$$\mathrm{2ArN{=}N{\cdot}OH \rightarrow ArN{=}N{\cdot}O{\cdot}N{=}NAr + H_2O}$$

$$\mathrm{ArN{=}N{\cdot}O{\cdot}N{=}NAr \rightarrow Ar^{\cdot} + N_2 + {}^{\cdot}ON{=}NAr}$$

Since water and nitrogen are produced and not nitrogen oxides, we suggest that homolysis of the N–O bond of the *aci* form of the nitramine occurs with the formation of a hydroxyl and an aryl diazotate radical (I). Aryl diazotate radicals have previously been shown to be intermediates in the Gomberg reaction[4] and in the thermal decomposition of *N*-nitrosoacylarylamines.[5] The observation by Bamberger,[6] which we have confirmed, that the decomposition of phenylnitramine in the presence of 2-naphthol gives benzene-1-azo-2-naphthol, supports the suggested formation of the diazonium hydroxide (II). Huisgen and Horeld have shown[7] in a similar way that phenyldiazoacetate is formed in the decomposition of *N*-nitrosoacylarylamines. The yield of nitrogen for decomposition in aromatic solvents was highest when the nitramine was 2,4,6-trisubstituted, thus precluding *C*-coupling of the diazonium hydroxide (II) with unreacted nitramine, a probable side-reaction in the decomposition of less substituted nitramines.

(*Received, January* 25*th*, 1968; *Com.* 094.)

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