MASTER

DECOMPOSITION OF HNS IN DMF

B. D. Faubion

DEVELOPMENT DIVISION

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Normal Process Development
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ABSTRACT

Three batches of HNS containing various amounts of DPE and TNB were heated in DMF for seven hours at 100, 120 and 148 C. Samples were withdrawn periodically and the relative percentages of the three constituents were determined by liquid chromatography.

At 100 and 120 C the relative percentage of HNS increased with time while the others diminished. At 148 C the opposite was observed. An additional material which has not been identified was also observed in the chromatograms of the materials heated at 148 C.

INTRODUCTION

The higher bulk density HNS II is produced by recrystallization of HNS I from DMF. During the recrystallization the temperature is normally kept below 110 C. At higher temperatures the solution becomes black and instances have been reported where the solution became self-heating. This study has been initiated to investigate the kinetics of decomposition of HNS in DMF.

EXPERIMENTAL

The reactions were carried out in a 150 ml round bottom flask fitted with a reflux condenser, stirrer and a thermocouple well. The flask was immersed in a 2-litre oil bath which was heated with a quartz immersion heater. The temperature was controlled with a proportional temperature controller with the sensing element immersed in the DMF. The temperature of the DMF was monitored using a thermocouple whose output was fed to a strip chart recorder. In all runs three grams of HNS was added to 100 ml of DMF. Three different samples of HNS were each run at 100, 120 and 148 C. Two of the samples had previously been analyzed by liquid chromatography. Lot 5173-1-11 was 98.63% HNS, 1.35% dipicrylethane (DPE) and 0.02% 1,3,5-trinitrobenzene (TNB). Lot 66-48 was 97.37% HNS, 2.63% DPE and less than 0.01% TNB. The third sample was prepared by adding approximately 10% by weight of DPE to Lot 66-48.

Approximately 1 ml of the reaction mixture was withdrawn after 1,3,5 and 7 hours. The DMF was evaporated in a vacuum oven at 60 C and the amount of recovered solid determined. The solid was then dissolved in p-dioxane to give a concentration of approximately 0.3 mg/ml. The solutions were then analyzed on the liquid chromatograph using the procedure reported by Schaffer(1). The samples prepared by adding DPE to Lot 66-48 were also analyzed at 0 hours.

(1) MHSMP-75-5G, "HNS Analysis," C. L. Schaffer, October - December 1974.

RESULTS AND DISCUSSION

The results of the liquid chromatograph analysis of the solids withdrawn from the DMF solutions are given in Tables I through IX. These results indicate that at 100 and 120 C the percentage of HNS relative to the other two materials increases with time. At 148 C the reverse is observed. Unfortunately the analytical procedure used does not measure the absolute amount of each material but rather the relative percentages normalized to 100%. This procedure also does not take into account other materials which may be present. This presents a problem in the interpretation of the decomposition kinetics. This is especially true for the 148 C runs, where an additional unidentified component was observed in the samples taken at 5 and 7 hours. The comparison of the chromatograms shown in Fig. 1 of the 1- and 7-hour samples withdrawn from the 148 C run on Lot 5173-1-11 illustrate the change in the sample and the appearance of the unknown material.

It is apparent from these preliminary experiments that there is considerable decomposition of HNS in DMF at 148 C; however, in order to determine the kinetics of decomposition, a method for the analysis of the absolute amounts of all materials present in the samples must be found. This can probably be accomplished by modifying the liquid chromatograph procedure if the unknown components can be isolated and identified.

FUTURE WORK

Isolation and identification of the decomposition products of HNS in DMF will be attempted. Modification of the liquid chromatograph method to give absolute instead of relative percentages will be considered.

Table I. Liquid Chromatograph Analysis of 5173-1-11
HNS from DMF at 100 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
1	99.9		
3	99.85	0.15	
5	99.9		
7	99.9		

Table II. Liquid Chromatograph Analysis of 5173-1-11
HNS from DMF at 120 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
1	99.9		
3	99.9		
5	99.9		
7	99.9		

Table III. Liquid Chromatograph Analysis of 5173-1-11
HNS from DMF at 148 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
1	99.9	< 0.1	< 0.1
3	99.9	< 0.1	< 0.1
5	99.67	< 0.1	< 0.1
7	98.9	0.39	0.72

Table IV. Liquid Chromatograph Analysis of 66-48 HNS
from DMF at 100 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
0	96.59	3.41	< 0.1
1	98.2	1.8	
2	98.06	1.9	
3	98.48	1.52	
4	98.85	1.15	
5	99.05	0.95	

Table V. Liquid Chromatograph Analysis of 66-48 HNS
from DMF at 120 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
1	98.6	1.4	< 0.1
2.5	99.41	0.35	0.24
4.5	99.9		
6.5	99.9		

Table VI. Liquid Chromatograph Analysis of 66-48 HNS
from DMF at 148 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
1	99.6	0.18	0.22
3	99.35	0.22	0.44
5	99.18	0.19	0.63
7	98.99	< 0.1	1.01

Table VII. Liquid Chromatograph Analysis of 66-48 HNS
with 10% DPE Added from DMF at 100 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
0	88.22	11.75	< 0.1
1	90.9	9.1	< 0.1
3	93.98	6.02	< 0.1
5	95.93	4.07	< 0.1
7	97.5	2.5	< 0.1

Table VIII. Liquid Chromatograph Analysis of 66-48 HNS
with 10% DME Added from DMF at 120 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
0	82.59	16.56	0.84
1	94.67	5.32	< 0.1
3	99.21	0.79	< 0.1
5	99.74	0.26	< 0.1
7	99.9	< 0.1	< 0.1

Table IX. Liquid Chromatograph Analysis of 66-48 HNS
with 10% DPE Added from DMF at 148 C

<u>Time (hr)</u>	<u>% HNS</u>	<u>% DPE</u>	<u>% TNB</u>
0	91.08	8.92	< 0.1
1	99.15	0.50	0.35
3	99.24	0.16	0.65
5	98.93	0.41	0.61
7	98.79	0.49	0.71

Fig. 1. Liquid Chromatograms of the HMS (5173-1-11) from DMF at 148 C. A. 1 Hr. B. 7 Hrs.