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DECOMPOSITION OF HEXANITROSTILBENE (HNS) IN DIMETHYLFORMAMIDE - AN NMR ANALYSIS

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DEVELOPMENT DIVISION

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Normal Process Development
Endeavor No. 107

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ABSTRACT

Isothermal aging of DMF solutions of crude HNS and concomitant monitoring of the reaction mixtures through NMR techniques, shows the system to behave in a similar manner from 95 through 116 C, with no apparent reaction anomalies occurring within this range. At the intermediate temperature studied (104.5 C), the decomposition of HNS occurring within the normal process time, is at such a low level as to not indicate any potential processing problems. However, the decompositional behavior of the major impurity, dipicrylethane, occurs in a relatively rapid fashion, some 500 times faster at 105 C than HNS for 50% decomposition.

EXPERIMENTAL

Previous NMR analysis of dimethylformamide (DMF) solutions of hexanitrostilbene (HNS) has shown that decomposition of the material does occur in this solvent(*1*). The rate of decomposition of high purity HNS is not of concern at this time, but the behavior of the crude material undergoing purification/recrystallization processing with DMF in the thermal range actually experienced during processing is of potential concern.

A 1 mℓ solution of HNS (Chemtronics Lot 66-48) in d-7 DMF (99.5 atom %), at a concentration of 12.0 mg per g of solvent, was placed in standard 5 mm x 7 inch NMR tubes and placed in a Kontes NMR tube sample concentrator for isothermal aging, with temperature variation < 1.0 C degrees. At selected elasped times, three samples were removed, tetramethylsilane (TMS) added for internal lock material, and the sample run on a Varian HA-100, employing routine integration techniques. The HNS aromatic and ethylenic protons (922 and 728 hz, respectively) were monitored, using the formyl proton resonance of the d-7 DMF as the internal quantitive standard. The possibility of proton/deuterium exchange was studied but was not indicated, particularly in view of the results obtained when HNS was treated in an identical manner using protonated, high purity DMF (Eastman, spectroquality). The decomposition of HNS, as indicated by the shrinking and eventual disappearence of the HNS aromatic and ethylenic resonances, while the formyl peak of DMF remained unchanged, followed the same behavioral pattern as seen with the deuterated solvent system. Repeated integration of the formyl and the d-5 n,n-dimethyl resonances (280 hz) produces the same peak ratio between the two, regardless of the sample and the extent of indicated decomposition. RF power and sweep parameters were maintained at constant settings for all samples to further normalize the results, and in order not to infuse anomalous saturation effects during the studies. The overall results show that the ratio of the formyl and d-5 dimethyl resonances remain essentially constant and the integration peak values for these two resonances do not appreciably change during the study, regardless of original unaged solution or one in which effectively total decomposition has taken place.

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(1) G. L. Clink, "Thermal Stability of Hexanitrostilbene (HNS) in N,N-Dimethylformamide (DMF)," MHSMP-76-5Q (October-December 1975).

Isothermally aged samples were produced from three different systems; 95, 104.5, and 116 C. The intermediate temperature was of main interest in that approximately 105 C is the normal recrystallization/purification process temperature. The results of NMR analyses of the three thermally aged systems are presented in Table I (95 C), Table II (104.5 C) and Table III (116 C). Graphic behavioral comparison of the three systems is presented in Fig. 1.

This study also attempted to estimate the behavior of three different lots of crude HNS during recrystallization/purification at 104.5 C. The three lots were obtained from three different sources. The sample group was comprised of the following,

Chemtronics Lot 66-48
Teledyne Lot 1126
United Technologies Corp. (UTC) Lot CSD/UT

Aging and analysis were performed in an identical manner as with the Chemtronics 66-48. The results are presented in Table IV and in Fig. 2. These clearly show the relatively slower rate of decomposition of the UTC material, with the Teledyne sample undergoing the most rapid breakdown, although not indicated as significantly greater than Chemtronics 66-48.

The following analytical results obtained from these three lots, were previously done by liquid chromatography at Pantex, and are presented for comparison purposes with the NMR generated rate results presented in Table IV and Fig. 2.

	Teledyne (1126)	UTC (CSD/UT)	Chemtronics (66-48)
Hexanitrostilbene (HNS, %)	93.3	98.5	97.3
Dipicrylethane (DPE, %)	6.7	1.5	2.6
Trinitrobenzene (TNB, %)	-	-	0.1
Melting Point (C)	311.2	315	313

Initial appraisal of the data indicates a sequential relationship between the rapidity of decomposition and the increasing percent of dipicrylethane present in the HNS sample. To obtain some idea of the decomposition behavior of dipicrylethane in DMF, a 9.0 weight percent solution was aged at 104.5 C, and processed in an identical manner as the previously studied HNS. The aromatic DPE resonance peak at 917 hz was monitored relative to the formyl resonance at 800 hz. The analytical results of these runs are presented in Table V.

It has been suggested that raw HNS be slurried for four hours at 70 C, in a 50/50 (V) solution of DMF/acetone, for the purpose of removing the bulk of dipicrylethane, trinitrobenzene, and other impurities in the raw material. Because the boiling point of this binary solvent is near the slurry temperature of 70 C, it was decided to study the decomposition behavior of a 9.0 wt %

solution of DPE in this solvent at 64 C (arbitrary), and also compare its behavior in DMF alone. The results of these runs are presented in Tables VI and VII, and in Fig. 3. The data indicate that at four hours, the DPE in DMF has decomposed approximately 2.6 times that in the DMF/acetone solution. Fig. 4 presents a semi-log plot of the decomposition of DPE in DMF at 64 and at 104.5 C and in DMF/acetone at 64 C. The decomposition curves of HNS and of DPE at the suggested processing temperature of approximately 105 C are presented in Fig. 5. An approximation from the data in Fig. 5 and the corresponding tables indicates that the 50% decomposition point for both materials occurs > 500 times more rapidly for DPE.

No in depth NMR spectral work has been done on the decomposition residues in these studies. HNS produces a dark brown sludge which is highly soluble in acetone. This material produces a spectrum which has a very low level of proton spectral resonance, with indication of several peaks between 900 to 1000 hz, and necessitates time averaging to obtain an intelligible spectra. This is being done at this time. The DPE residue, highly soluble in acetone, produces a much higher level of proton resonance, but due to the high RF levels needed to obtain coherent signals, will be time averaged as is the HNS residue. Spectra of the DPE system are presented in Fig. 6. Fig. 6a is that of the unheated, freshly prepared DPE in d-7 DMF. Fig. 6b is that of the DPE residue obtained at 64 C in 4 hours. A 250 hz expanded sweep of the 800 to 1000 hz region of 6b is presented in 6c. The prominent down field tenting effect of the several doublets is largely due to the high RF levels necessary to obtain the spectrum.

COMMENTS

The data obtained in this study were not for the purpose of determining specific kinetics parameters, i.e., rate constants, as the material is not of high purity (> 99.9%). The data merely give an empirical appraisal of the decompositional behavior of typical HNS production lots, as they might relate to actual production practice. However, the decomposition of high purity HNS will be studied in the immediate future to ascertain any anomalous behavior due to the absence of impurities. It is interesting to note, in the case of the HNS study at 95, 104.5, and 116 C (Fig. 1), how well the increased rate of decomposition with increased temperature approximates the Le Chatelier's prediction of doubling for each 10° rise. An attempt will be made to obtain spectra of both the HNS and DPE isothermal residues for purposes of possible identification of the products.

Table I. HNS Decomposition in DMF (95 C)

(12.0 mg/g)

Elapsed Time (hrs)	Percent HNS Decomposed				
	1	2	3	Avg.	σ
0	0	0	0	0	0
74	3.4	3.4	3.2	3.3	0.12
165	9.6	9.6	9.4	9.5	0.12
193	12.4	12.6	12.4	12.5	0.12
359	26.4	26.2	26.5	26.4	0.15
455	41.0	40.8	41.2	41.0	0.20
550	46.6	46.7	46.4	46.6	0.15
645	61.2	61.4	61.2	61.3	0.12
716	64.0	63.8	64.0	63.9	0.12
790	78.3	78.3	78.6	78.4	0.17

Table II. HNS Decomposition in DMF (104.5 C)

(12.0 mg/g)

Elapsed Time (hrs)	Percent HNS Decomposed				
	1	2	3	Avg.	σ
0	0	0	0	0	0
23	5.5	5.6	5.6	5.6	0.06
47	9.4	9.6	9.6	9.5	0.12
71	12.8	12.8	12.9	12.8	0.06
143	29.0	29.2	29.2	29.1	0.12
167	32.9	33.1	33.1	33.0	0.12
215	47.0	47.1	46.9	47.0	0.10
239	54.0	54.2	54.2	54.1	0.12
311	63.6	63.8	63.6	63.7	0.12
395	79.9	80.1	79.8	79.9	0.15

Table III. HNS Decomposition in DMF (116 C)

(12.0 mg/g)

Elapsed Time (hrs)	Percent HNS Decomposed				
	1	2	3	Avg.	σ
0	0	0	0	0	0
2	0.5	0.7	0.7	0.6	0.11
5	4.5	4.7	4.5	4.6	0.12
27	8.9	8.9	9.1	9.0	0.12
44	11.7	11.9	11.7	11.8	0.12
51	13.2	13.4	13.4	13.3	0.12
72	22.1	22.3	22.3	22.2	0.12
164	61.3	61.5	61.6	61.5	0.15
211	77.0	77.2	77.2	77.1	0.12

Table IV. Decomposition of Various HNS Lots in DMF (104.5 C)

(12.0 mg/g)

HNS Lot	Elapsed Time (hrs)	Percent HNS Decomposed				
		1	2	3	Avg.	σ
Chemtronics 66-48	0	0	0	0	0	0
	23	5.5	5.6	5.6	5.6	0.06
	71	12.8	12.8	12.9	12.8	0.06
	143	29.0	29.2	29.2	29.1	0.12
	239	54.0	54.2	54.2	54.1	0.12
UTC/IB	0	0	0	0	0	0
	23	2.2	2.1	2.2	2.2	0.06
	71	11.2	11.2	11.4	11.3	0.12
	143	19.6	19.4	19.4	19.5	0.12
	239	34.2	34.8	35.3	35.1	0.26
Teledyne IB	0	0	0	0	0	0
	23	7.1	7.3	7.3	7.3	0.12
	71	15.5	15.5	15.3	15.4	0.12
	143	35.8	35.6	35.8	35.7	0.12
	289	58.0	58.2	58.2	58.1	0.12

Table V. Decomposition of Dipicrylethane in DMF (104.5 C)

Elapsed Time (hrs)	Percent DPE Decomposed				
	1	2	3	Avg.	σ
0	0	0	0	0	0
0.42	50.9	50.6	51.0	50.8	0.21
0.67	67.3	67.1	67.4	67.3	0.15
0.92	74.5	74.5	74.7	74.6	0.12
1.58	81.7	81.9	82.0	81.9	0.15

Table VI. Decompoosition of Dipicrylethane in DMF (64 C)

(9.0 Wt. %)

Elapsed Time (hrs)	Percent DPE Decomposed				
	1	2	3	Avg.	σ
0.0	0	0	0	0	0
1.0	19.0	18.8	19.1	19.0	0.15
2.0	28.2	28.0	28.3	28.2	0.15
3.0	38.4	38.4	38.1	38.3	0.17
4.0	47.2	46.8	47.1	47.0	0.21

Table VII. Decomposition of Dipicrylethane in DMF/Acetone (64 C)

(50/50 V/V)

Elapsed Time (hrs)	Percent DPE Decomposed				
	1	2	3	Avg.	σ
0.0	0	0	0	0	0
1.0	8.1	8.0	7.9	8.0	0.10
2.0	11.4	11.2	11.2	11.3	0.12
3.0	14.1	14.3	14.1	14.2	0.12
4.0	18.1	17.8	17.8	17.9	0.17

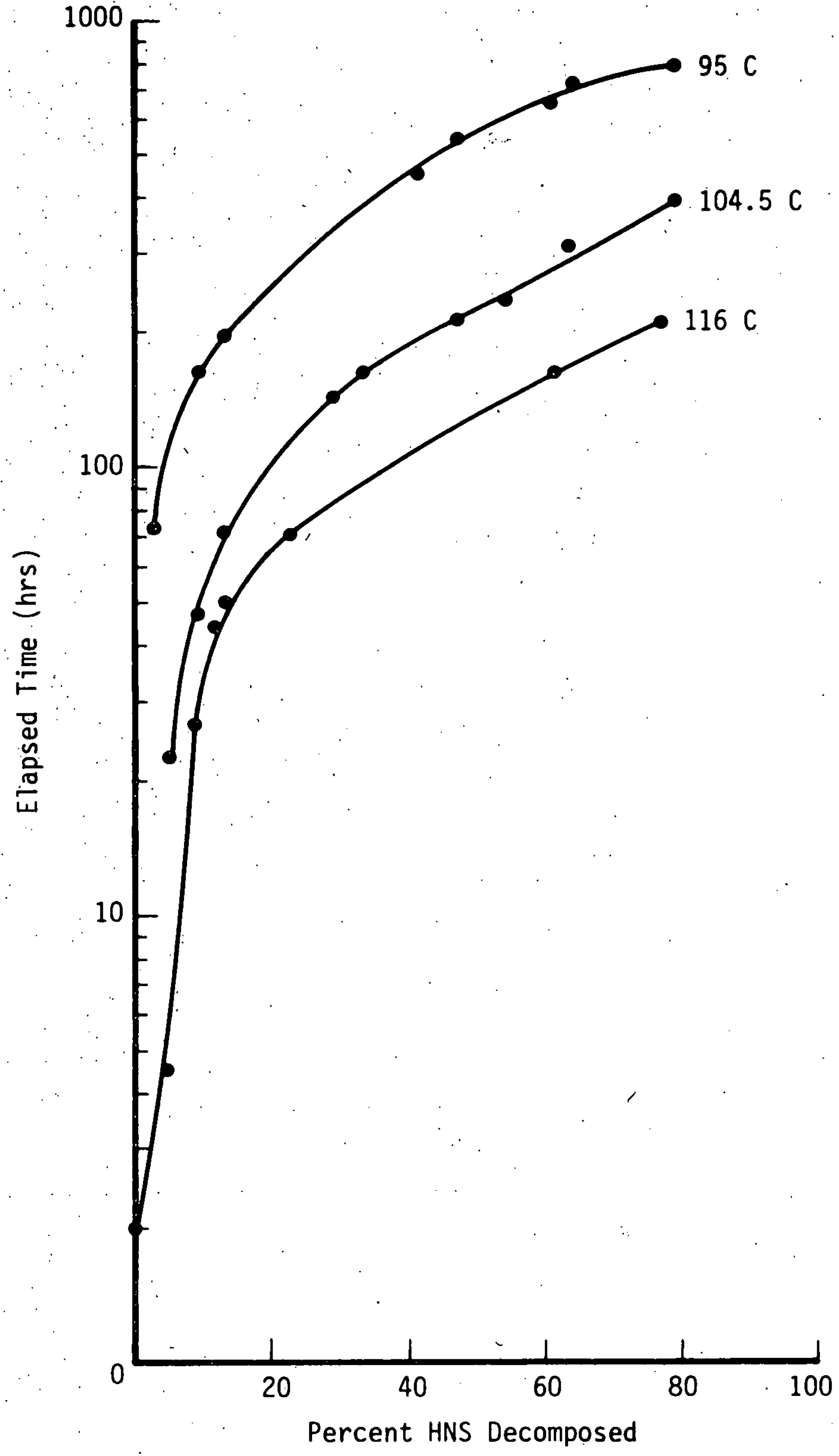


Fig. 1. Decomposition of HNS (Chemtronics 66-48) in DMF

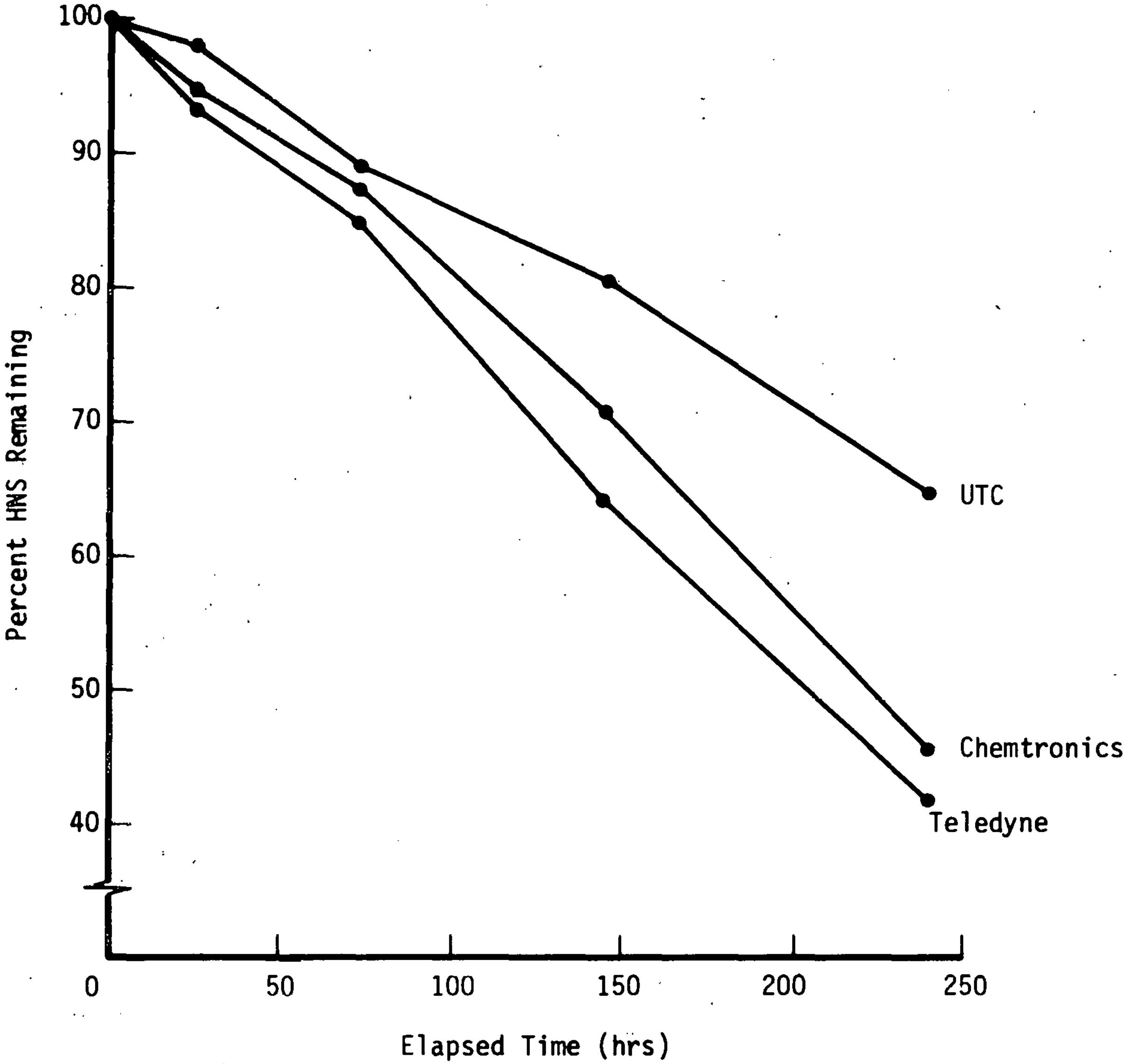


Fig. 2. Comparison of HNS Decomposition at 104.5 C (12.0 mg/g; d^7 DMF)

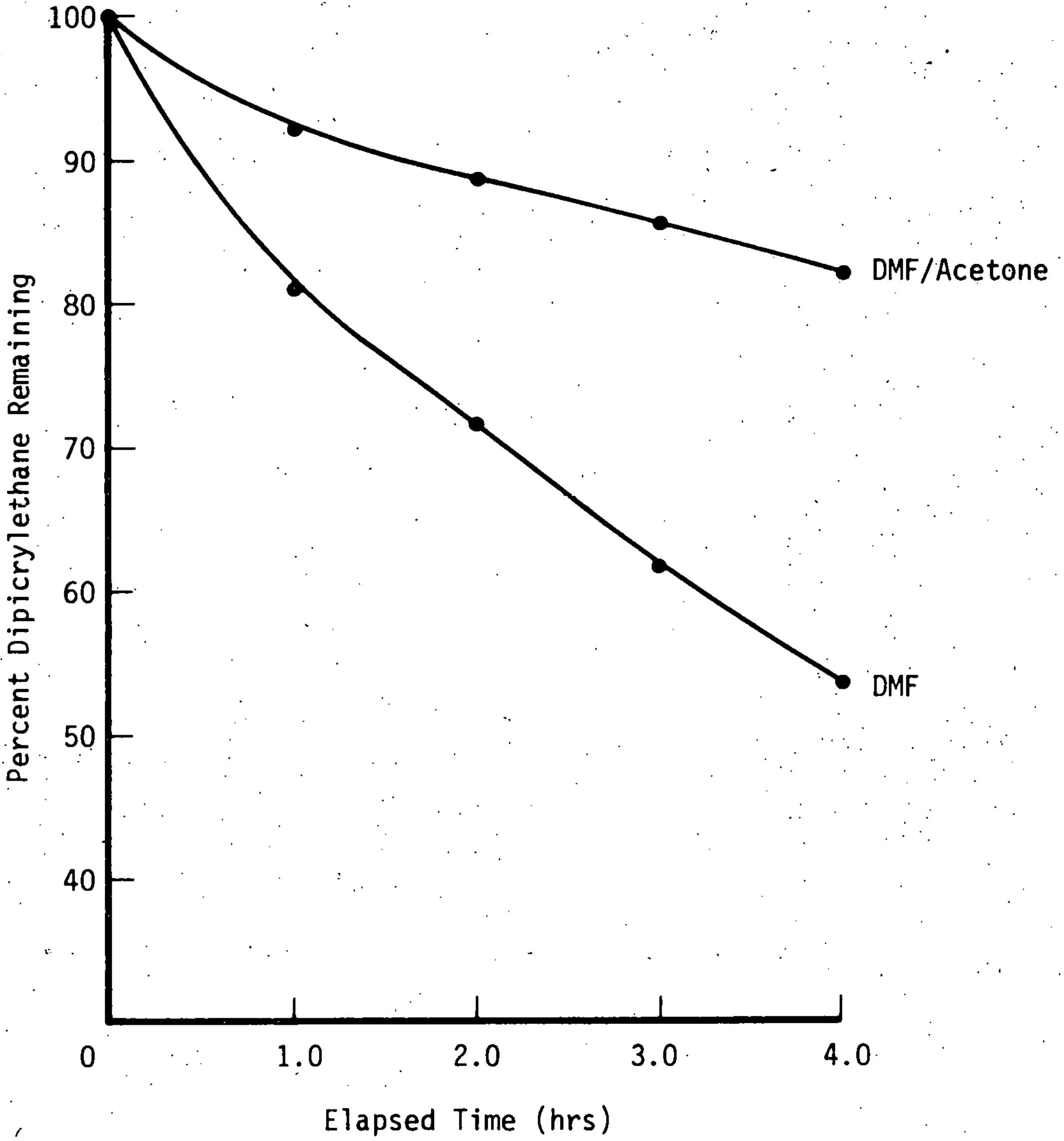


Fig. 3. Decomposition of Dipicrylethane in DMF and in DMF/Acetone at 64 C

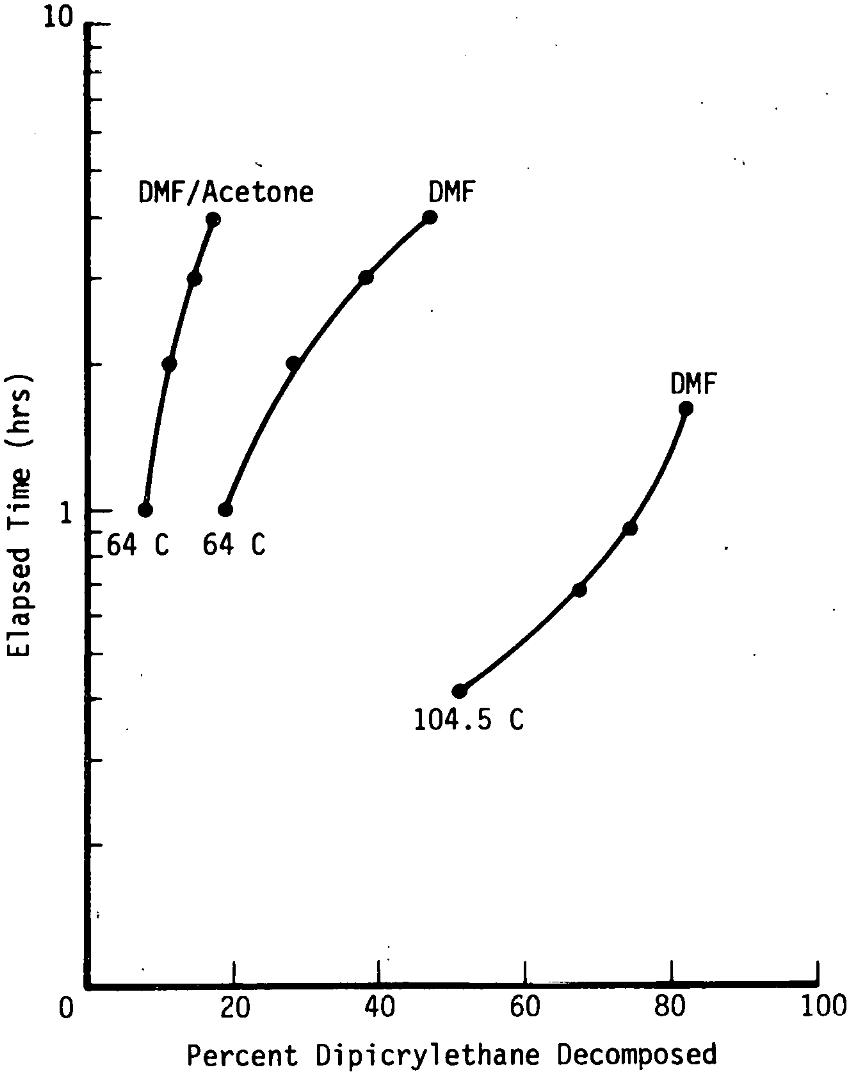


Fig. 4. Decomposition of Dipicrylethane in DMF and in DMF/Acetone Solutions

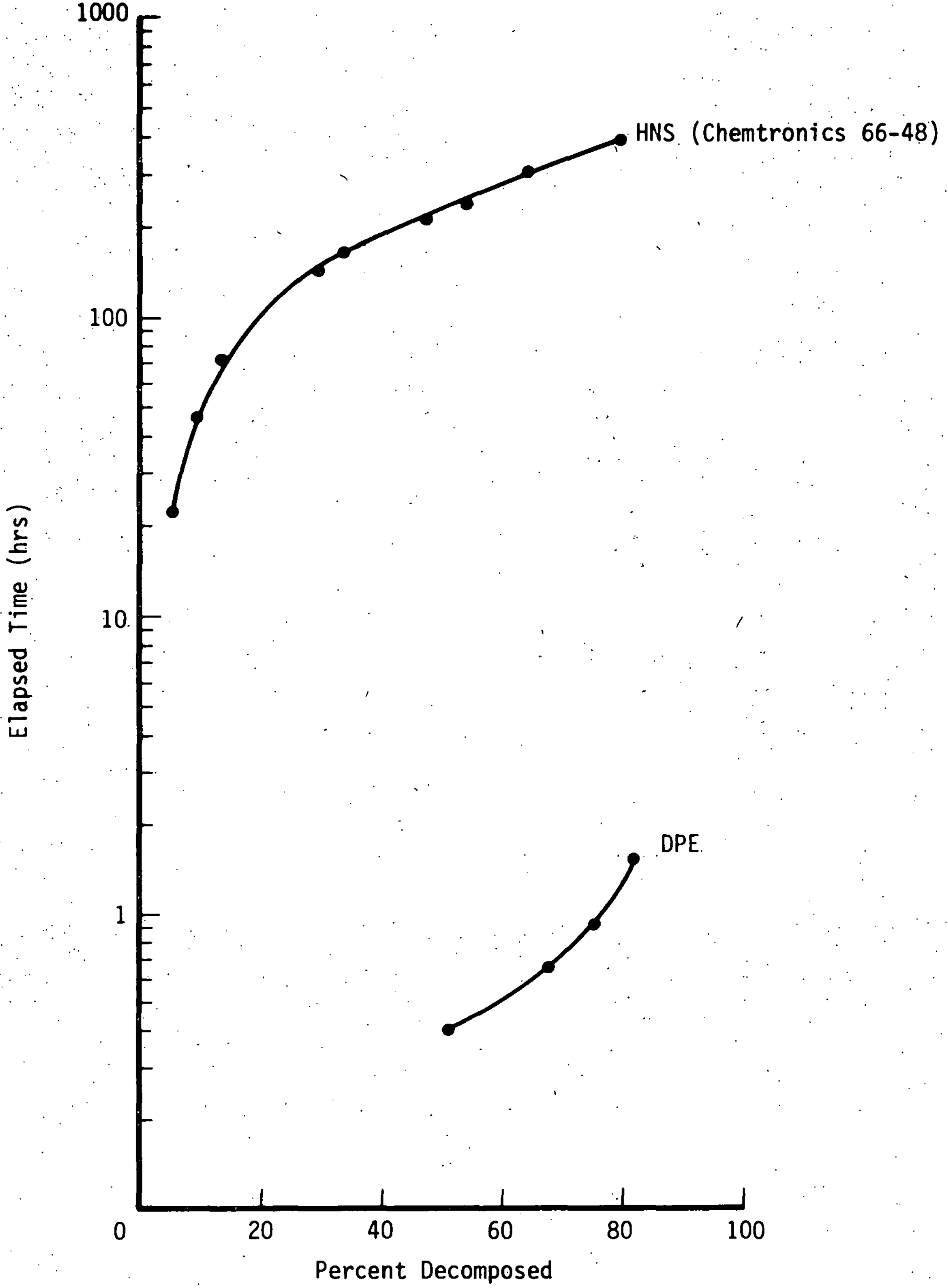
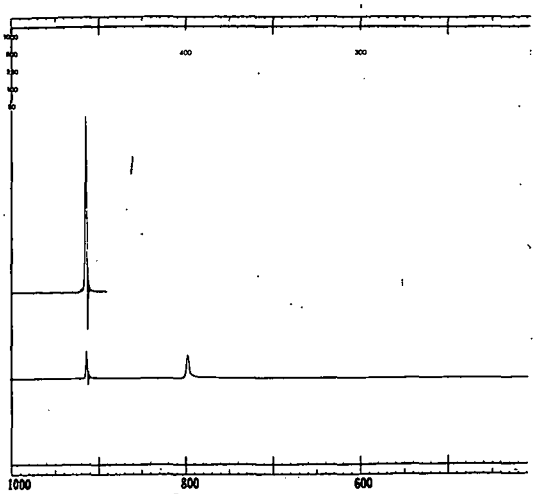
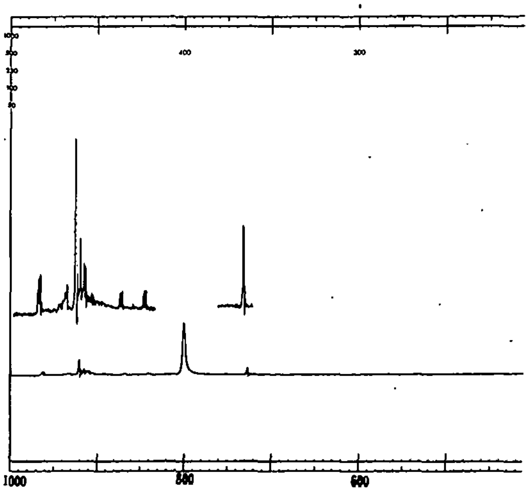


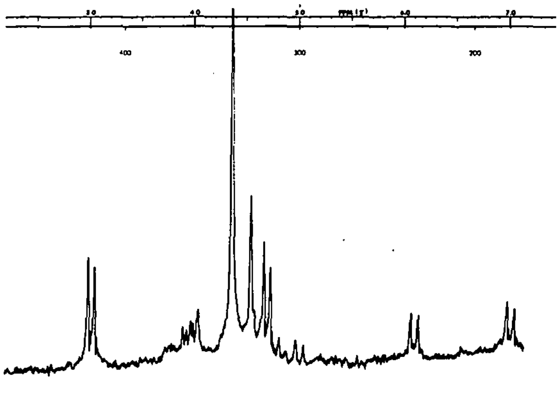
Fig. 5. Decomposition of HNS and of DPE in DMF at 104.5 C



A. Unaged



B. 64 C, 4 Hours



C. 250 hz Expanded, 800 to 1000 hz

Fig. 6. HA-100 Spectra of the Dipicrylethane System