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THERMAL STABILITY OF HEXANITROSTILBENE (HNS) IN N,N-DIMETHYLFORMAMIDE (DMF)

G. L. Clink

DEVELOPMENT DIVISION

OCTOBER - DECEMBER 1975

Normal Process Development
Endeavor No. 107

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ABSTRACT

A preliminary study of the thermal stability of HNS in DMF, at both ambient (21 C) and 120 C, has shown that the solute is decomposed in DMF. Additional work to establish the rate of decomposition in the temperature range of processing (90 to 110 C) is underway at this time. NMR spectral analysis through peak integration is employed to monitor the system.

DISCUSSION

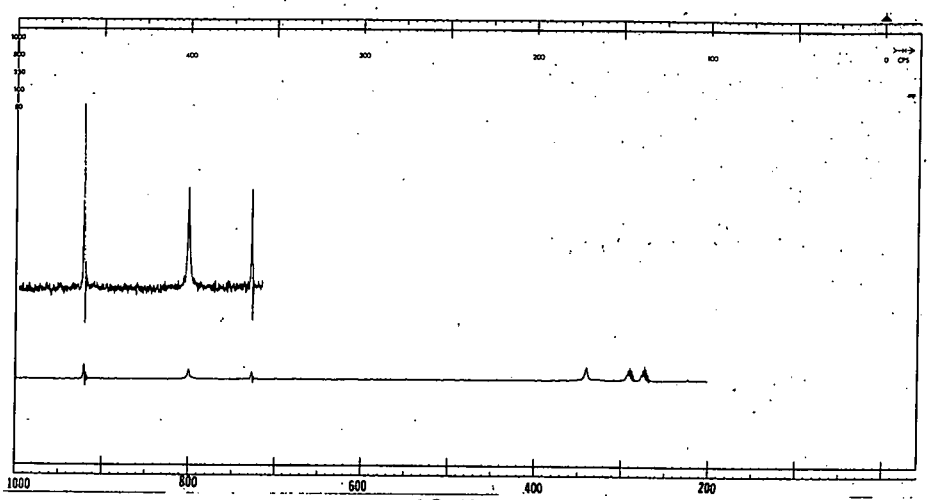
To study the thermal stability of HNS in DMF (the situation occurring in the recrystallization/purification process), saturated solutions of these two materials were isothermally aged at 21 C and at 120 C for extended periods of time. Samples were periodically removed and analyzed in a routine manner on a Varian HA-100, employing spectral peak integration techniques.

Saturated solutions of HNS (Sandia Lot 15-62-5) in deuterated DMF (d-7, Merck, 99.5 atom percent), were placed in standard 5 mm NMR sample tubes, and placed in a Kontes NMR sample concentrator maintained at 120 C. A second set of samples was isothermally aged at room temperature in the NMR laboratory (21 C). The individual samples were allowed to isothermally age prior to addition of TMS (internal lock) to the sample for analysis.

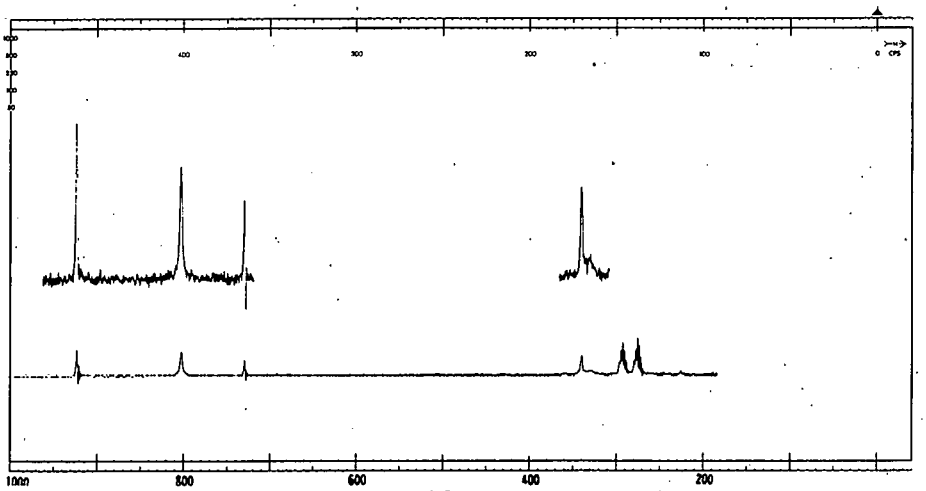
NMR analyses of the isothermally aged solutions are based on the integration of the HNS aromatic protons ($\sim$ 924 Hz) and the formyl proton of the d-7 DMF (803 Hz). Fig. 1 contains the spectra of the 21 C system, at 18 hours and at 2800 hours. The peak at 725 Hz is due to the HNS ethylene protons. The deutero dimethyl doublet is seen at approximately 280 Hz. The peak at approximately 340 Hz is due to water. Visual inspection of the spectra shows the rather obvious decline of the aromatic and olefinic proton peaks of HNS, relative to the formyl peak of DMF. Integration curves are not presented on the spectra, as the integrations are obtained through digital printout. The concentration of HNS in the 21 C system decreased from 12.6 mg/mℓ to 10.6 mg/mℓ at 2800 hours.

In the 120 C system (Fig. 2), the HNS concentration has decreased from 12.6 mg/mℓ to 1.3 mg/mℓ at 90 hours. At 120 hours, there is no spectral indication for the presence of HNS in the system, bearing in mind inherent sensitivity limits of the instrument.

As this study was of an exploratory nature to determine if HNS is, in fact, decomposed in DMF, the foregoing data must be considered somewhat empirical in nature. What the decomposition product(s) may be under these conditions (21, 120 C) is conjecture but the HNS/DMF system, when heated to 149 C, produces a tar-like polymeric substance (Fig. 3).

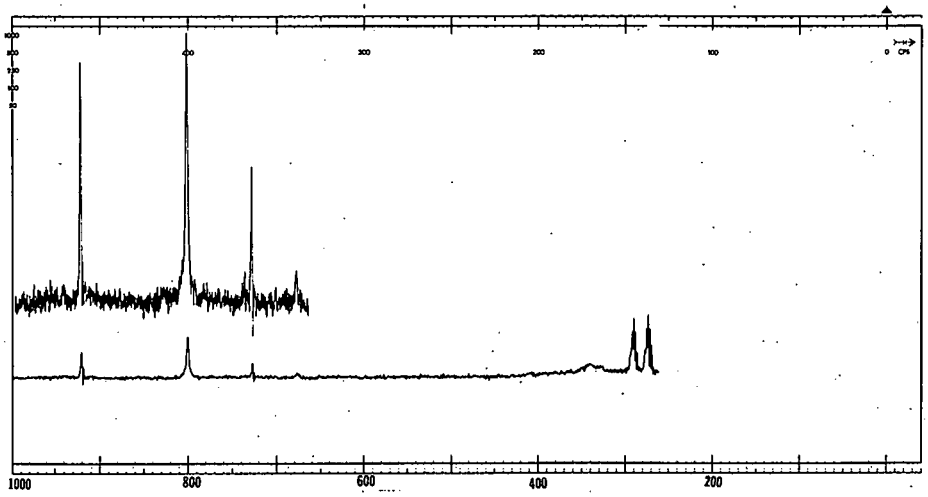


18 Hours

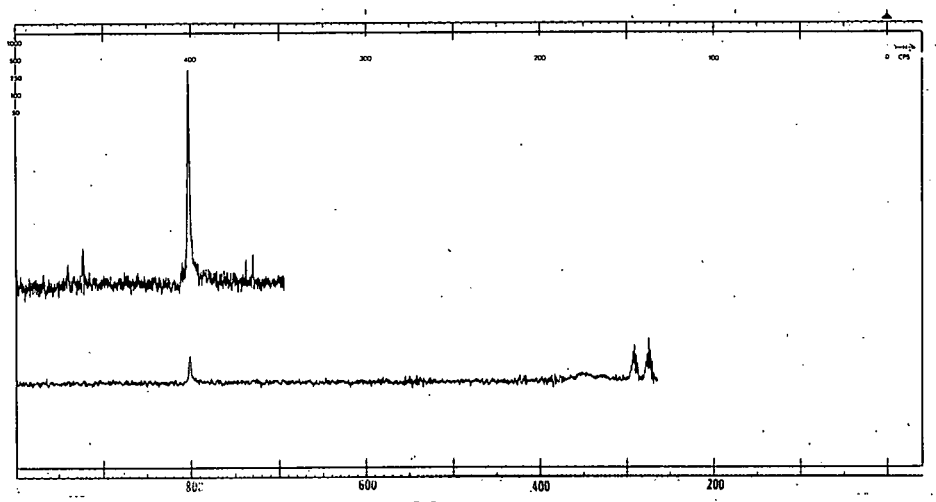


2800 Hours

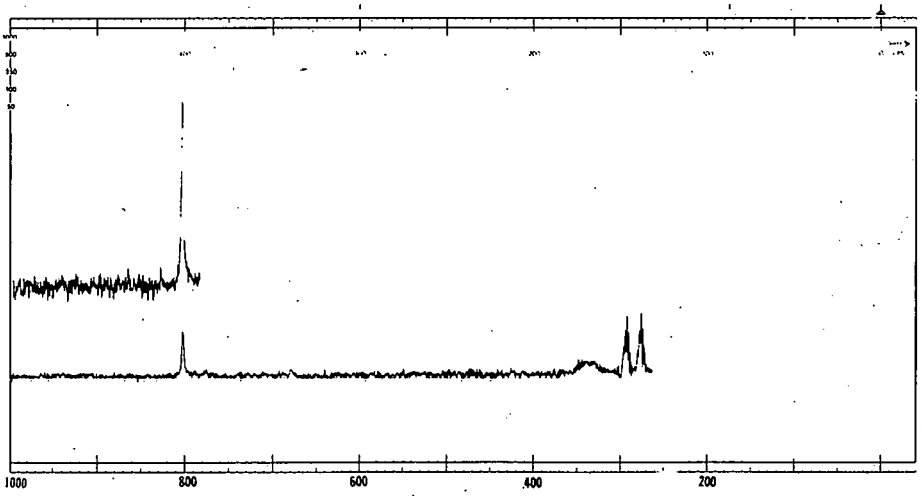
Fig. 1. HA-100 Spectra of HNS/DMF Solutions (21 C)



67 Hours



90 Hours



120 Hours

Fig. 2. HA-100 Spectra of HNS/DMF Solutions (120 C)

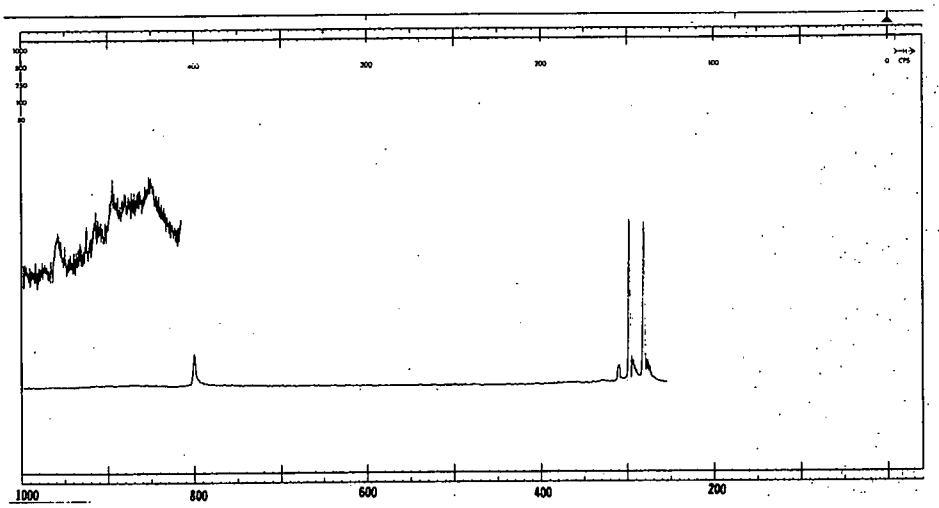


Fig. 3. HA-100 Spectrum of HNS/DMF Heated to 149 C

COMMENTS

Because the temperature range of practical interest is near 104 to 105 C (suggested recrystallization process temperature), a controlled study of the HNS/DMF system at 90, 100, and 110 C is underway to determine the actual rate of decomposition of the material.