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THE THERMAL DECOMPOSITION OF STYRENE-CO-ACRYLONITRILE TRIMERS TO FORM 2-AMINO-3-METHYL-1-NAPHTHALENECARBONITRILE

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ABSTRACT

During the spontaneous copolymerization of styrene and acrylonitrile, many different trimer structures are formed. Some of the trimers contain two acrylonitrile units and one styrene unit (An_2S). These trimers are composed of three pairs of *cis-trans* diastereomers, all having a 1-substituted-4-cyanotetralin nucleus. Two of the *cis-trans* pairs have been found to decompose upon heating resulting in the formation of 2-amino-3-methyl-1-naphthalenecarbonitrile. The mechanism of this rearrangement involves the elimination of ethylene *via* a retro Diels-Alder reaction. Kinetic investigations show that the reaction is first order in An_2S trimer.

INTRODUCTION

During the spontaneous polymerization of styrene, a variety of oligomer structures are formed. Many researchers over the past forty years have worked to identify the structures of these oligomers in an effort to gain information regarding the mechanism of initiation of the spontaneous polymerization of styrene.[1,2] More recently, the mechanism of spontaneous copolymerization of styrene (S) and acrylonitrile (An) has been investigated. Again, the structures of the oligomers were determined and used as evidence to determine the mechanism of initiation.[3,4] The structures and stereochemistry of the trimers containing two An and one S unit (An_2S) recently have been determined.[4] The results (Figure 1) indicate both diastereomers (*cis* and *trans*) of 4-cyano-1,2,3,4-tetrahydro-1-naphthalene-propionitrile (THNP), and both diastereomer pairs of 4-cyano-1,2,3,4-tetrahydro-α-methyl-1-naphthaleneacetonitrile (THNA) are formed. The ratios of the three *cis/trans* pairs of isomers THNP:S-THNA: R-THNA are

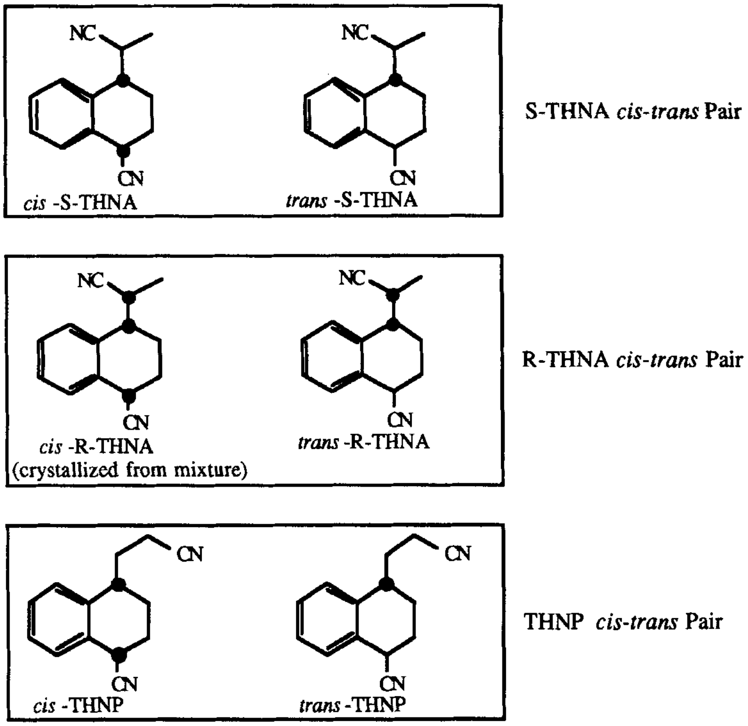
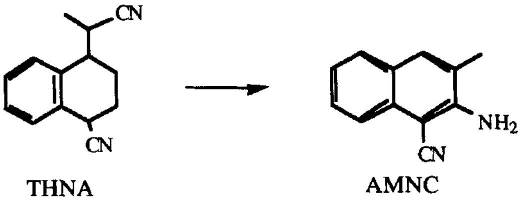


Figure 1 Structures of the An_2S trimers formed during the spontaneous copolymerization of styrene and acrylonitrile.

approximately 2 : 3 : 2, respectively. Approximately equal amounts of *cis* and *trans* diastereomers are formed within each pair.

During the study of the mechanism of formation of these trimers,[4] they were heated to gain further insight into their mechanism of formation. That experiment resulted in the discovery of a novel decomposition reaction of THNA producing a highly UV absorbing and fluorescing 1,2,3-trisubstituted naphthalene derivative [2-amino-3-methyl-1-naphthalenecarbonitrile (AMNC)] (Scheme 1). Since styrene-co-acrylonitrile is a key component in many plastics utilized in applications where UV stability is important, it was felt worthwhile to investigate the mechanism of AMNC formation.

In this paper the mechanism and kinetics of AMNC formation are investigated.



Scheme Formation of AMNC during thermal decomposition of THNA.

EXPERIMENTAL

Gas Chromatographic (GC) Analysis

Pyrolysis kinetics of the trimers was followed by GC analyses performed using a Hewlett Packard 5890A equipped with a flame ionization detector and a 0.25 mm X 30 m (0.25 mm film thickness) DB-17 (100 % methylphenylpolysiloxane) capillary column. The oven temperature was controlled at 230 °C for 10 min and then ramped at 5 °C/min to 280 °C.

Formation and Characterization of 2-Amino-3-Methyl-1-Naphthalene Carbonitrile (AMNC) and Ethylene From Pyrolysis of *cis*-4-Cyano-1,2,3,4-Tetrahydro-α*R*-Methyl-1-Naphthalene Acetonitrile (*cis*-R-THNA).

One gram of pure (double recrystallized from toluene) *cis*-R-THNA (m.p. = 112 °C) was sealed (*in vacuo*) in a glass ampoule. The ampoule was heated for two days in a sand bath set at 280 °C. The ampoule was removed, cooled to ambient temperature, and the end containing the brown pyrolysate was further cooled until it became too viscous to flow readily. Then, the other end was frozen to liquid nitrogen temperatures. A solid froze out, which liquified to a clear, colorless liquid, and finally vaporized well below ambient temperature. The gas was refrozen, the tube was opened, and the frozen gas was dissolved in $CDCl_3$ and found to be ethylene by ^1H NMR (s, 5.40 ppm) and ^{13}C NMR (123.0 ppm). The viscous brown syrup was flash chromatographed on 60 Å 230-400 mesh silica gel (Merck) with hexane:ethyl acetate 10:1, programming up to 4:1. The amber AMNC fraction was repeatedly recrystallized from chloroform to form pale yellow needles (m.p.=102 °C). The crystals were characterized by ultraviolet, infrared, ^1H NMR, ^{13}C NMR, and mass spectroscopic techniques and found to be 2-amino-3-methyl-1-naphthalenecarbonitrile.

Kinetic Pyrolysis of *cis*-R-THNA

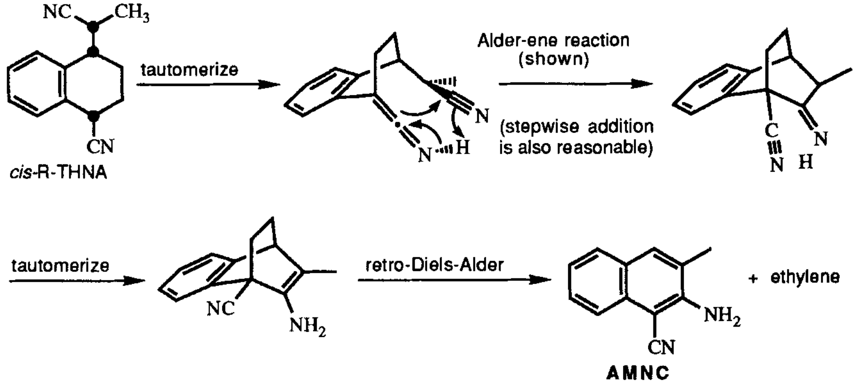
Kinetic pyrolyses were performed by dissolving *cis*-R-THNA in diphenylmethane (25/75 % w/w) and sealing the mixture in silanized glass tubes (*in vacuo*). The tubes were then placed in molten salt (40/7/53 % w/w/w $NaNO_2/NaNO_3/KNO_3$) at 265 °C. A tube was removed periodically and the contents analyzed by GC. The diphenylmethane served as both a solvent and internal standard. Diphenylmethane was found to be thermally stable under the conditions of the experiment.

RESULTS AND DISCUSSION

The oligomers were vaporized from SAn polymer *in vacuo* at 240 °C, condensed, and solvent fractionated (as previously described)[4] to obtain a mixture of the An_2S trimers. Upon standing, white crystals began forming in the purified An_2S mixture. X-ray crystallography studies showed that the compound was *cis*-4-cyano-1,2,3,4-tetrahydro-αR-methyl-1-naphthaleneacetonitrile (*cis*-R-THNA).

The proposed mechanism for AMNC formation from the trimer mixture is shown in Scheme 1. The crystalline trimer *cis*-R-THNA is shown as the starting material. The mechanism has the following features:

- The reaction is first order in trimer.
- The tautomerizations should be both acid- and base-catalyzed.
- The Alder-ene reaction is not necessarily acid- or base- catalyzed, but a bimolecular version of the cyclization would surely be so catalyzed.
- Because of the equilibria brought about by the tautomerizations, any of the THNA isomers should be able to produce AMNC. The *cis*/*trans*-R-THNA pair might decompose at a slightly different rate than the *cis*/*trans*-S-THNA pair. This is because the two stereogenic centers (the α- and 1- centers) retain their integrity until the second tautomerization. Within each *cis*/*trans* pair, both *cis* isomers should yield AMNC at the same rate as the *trans*, because that stereogenic center (the 4- center) is lost in the ketenimine intermediate.
- The *cis*/*trans*-THNP pair cannot form AMNC by this mechanism.
- Ethylene is predicted as a by-product of the reaction.



Scheme 1 Proposed Mechanism for AMNC Formation.

In order to test the fundamentals of the mechanism, *cis*-R-THNA was pyrolysed at 280 °C in evacuated and sealed glass ampoules. ^{1}H and ^{13}C NMR confirmed the formation of ethylene.

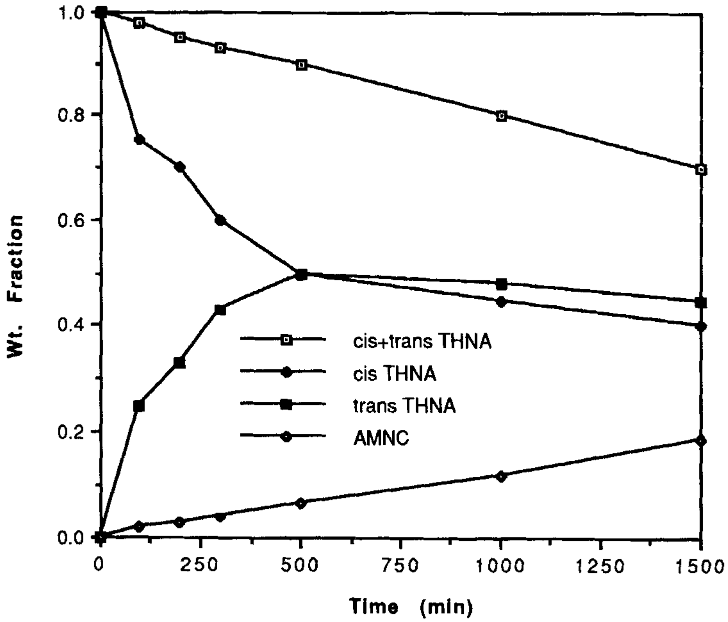


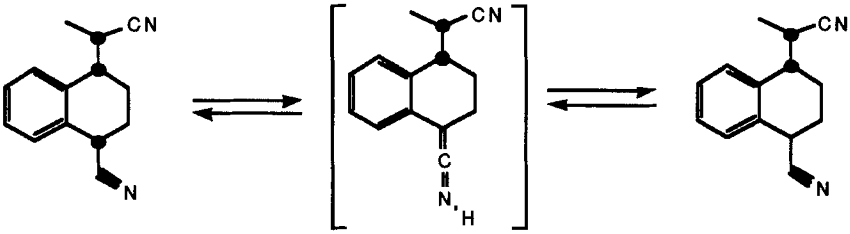
Figure 2 Epimerization and rearrangement kinetics of *cis*-R-THNA at 280 °C.

Kinetic studies were performed in silanized, evacuated, and sealed glass ampoules in the presence of diphenylmethane as an internal standard. A typical graph (wt fraction vs. time) showing the loss of the crystalline trimer *cis*-R-THNA and the formation of products (GC analysis) during pyrolysis at 280 °C is shown in Figure 2.

The starting trimer *cis*-R-THNA does indeed decay, and AMNC is produced. However, the major initial product is its corresponding *trans* diastereomer. The epimerization reaction is much more facile than the formation of AMNC. In fact, the epimerization reached equilibrium before 10 % AMNC had been formed. Since both *cis* and *trans*-R-THNA can produce AMNC, the decomposition of their sum (the *cis+trans* curve in Figure 2) was monitored for decay.

Trace amounts (less than 1 % of the reaction mixture) of several other products are also observed. The other pair of THNA diastereomers (namely, *cis* and *trans*-S-THNA) slowly form. Also, propionitrile and 1-cyanonaphthalene are detected. These four trace products, along with AMNC, all increase monotonically under these conditions.

These observations are consistent with the predictions of Scheme 1, according to the isomerization pathways described below. The *cis-trans* isomerization should proceed through the same ketenimine intermediate required for AMNC formation (Scheme 1). Instead of proceeding on toward AMNC, the reverse-tautomerization occurs (Scheme 2), scrambling the stereochemistry at the 4-position.

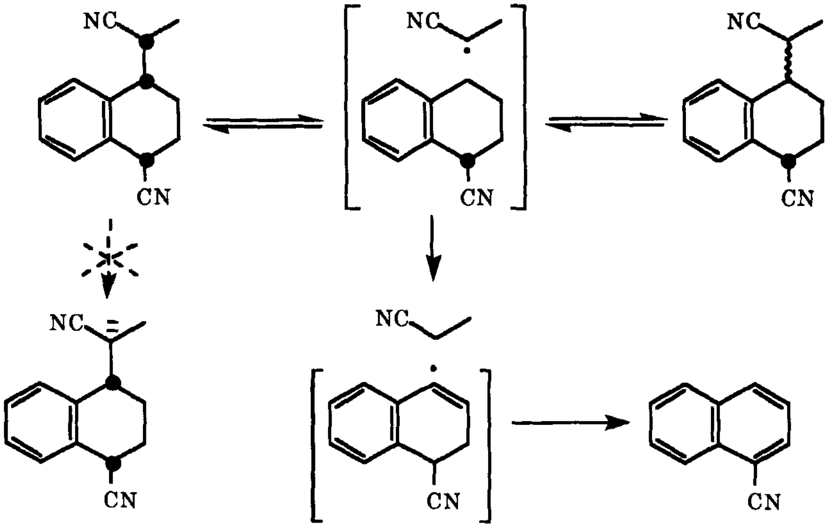


Scheme 2. Proposed *cis-trans* isomerization mechanism of *cis*-R-THNA.

The much slower epimerization which interconverts R-THNA with S-THNA, conceivably could occur through a similar mechanism; i.e., tautomerization through the labile α-nitrile proton. This process should be slower than the *cis-trans* isomerization of Scheme 2, since this proton is less labile and the ketenimine is not conjugated to the aromatic ring. However, another pathway is more likely. The molecule can cleave between the adjacent stereogenic carbons to form a radical pair, which then recloses to randomize the stereochemistry about the broken/reformed bond (Scheme 3). Additional evidence for this pathway lies in the recovery and characterization of both 1-cyanonaphthalene and propionitrile from the pyrolysis. These products should be readily available by means of a disproportionation reaction (hydrogen abstraction) of the radical pair, followed by the loss of a hydrogen molecule as shown in Scheme 3.

Figure 3 shows the rate plots [ln(%conv.) vs. time] for the data in Figure 2. The initial loss of *cis*-R-THNA trimer is an order of magnitude faster than the initial loss of total trimer. Two conclusions can be drawn. First, since the *cis-trans* isomerization passes through the same intermediate as does the first step of the AMNC formation mechanism, this first step cannot be the rate-limiting step. Otherwise, the two processes would have the same rate. Second, the later points in the graph for the loss of trimer begin to fall below the line. This implies a rate constant increase. A reasonable interpretation of this involves autocatalysis; i.e., a product of the reaction catalyzing the reaction which forms it.

Four temperatures were chosen (280 °C, 263 °C, 240 °C, and 230 °C). Several pyrolyses were performed at each temperature, and concentration vs. time effects were determined for each reaction component in analogy to the kinetic analyses described above for 280 °C. At each temperature, the *cis-trans* epimerization is much faster



Scheme 3 Proposed R-S epimerization mechanism of *cis*-R-THNA.

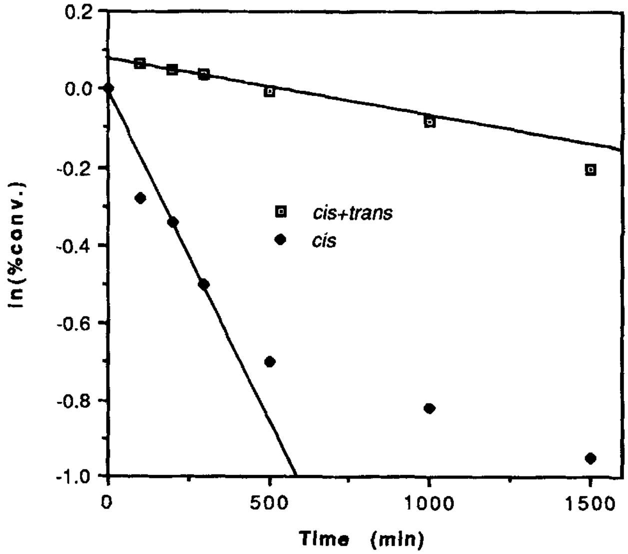


Figure 3 Comparison of rate of total loss of R-THNA *cis-trans* pair with the loss of *cis*-R-THNA at 280 °C

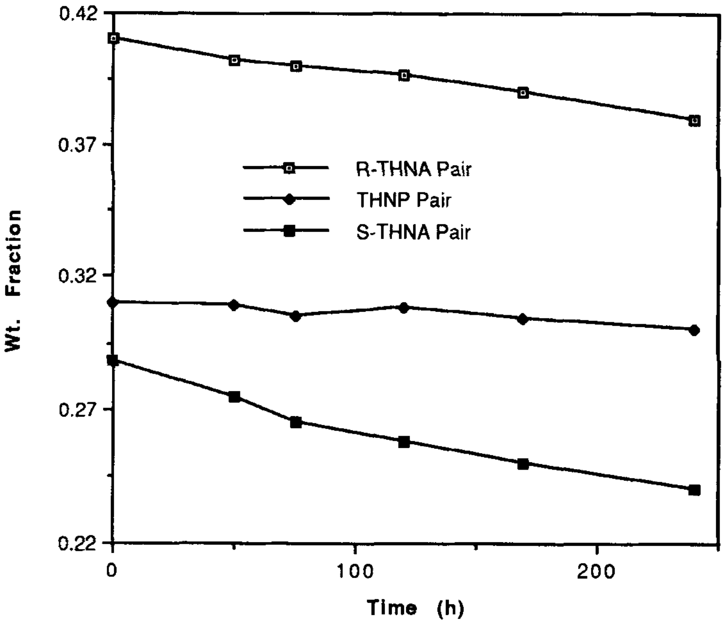


Figure 4 Pyrolysis of the An_2S trimer mixture at 230 °C: loss of the three diastereomer pairs vs time.

than the decomposition of the trimers to AMNC. The processes derived from bond cleavage (propionitrile and 1-cyanonaphthalene formation, as well as the build-up of the S-THNA pair of epimers) can only be monitored at higher temperatures since they are almost undetectable at or below 240 °C.

However, the rate constants used to obtain the Arrhenius activation parameters (Table 1) are taken instead from the kinetic pyrolyses of the An_2S trimer mixture. There, the decay rates of each of the trimers were generated "*in situ*," and can be more readily compared.

The An_2S trimer syrup was pyrolyzed under conditions analogous to those used for the purified crystalline trimer. Figure 4 shows the resulting trimer decay vs. time at 230 °C for each diastereomer pair. AMNC is (by far) the major product observed. It appears that both pairs of THNA diastereomers decompose to AMNC as their major product, while the THNP diastereomer pair decomposes very slowly, if at all.

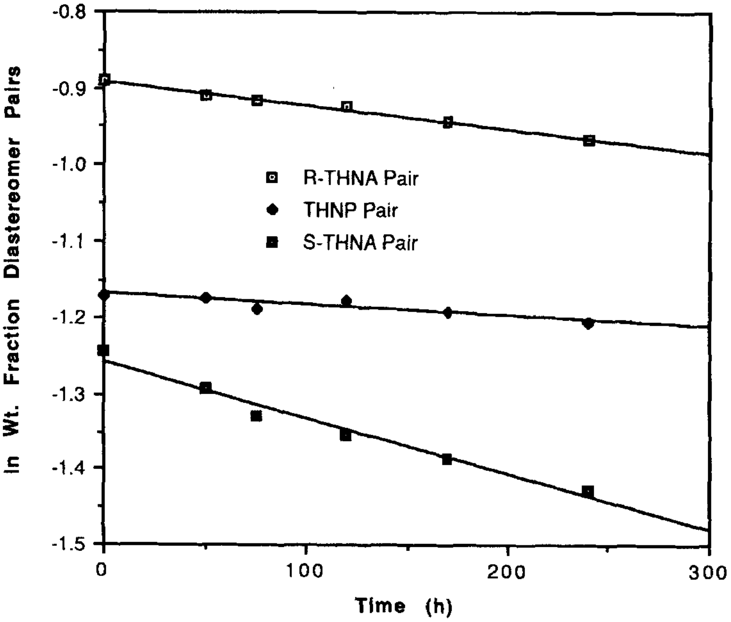


Figure 5 Relative rates of loss of the three An_2S trimer *cis-trans* pairs at 230 °C.

TABLE 1
The Arrhenius Activation Parameters.

Trimer	E_a	log A
S-THNA	32.0	7.2
R-THNA	31.1	6.6
THNP	31.2	6.1

The relative rates of decay of the three diastereomer pairs are shown in Figure 5. The S-THNA pair decomposes over 50 % faster than the R-THNA pair, and almost an order of magnitude faster than the THNP pair. Because of the low conversion of the THNP isomers, it is not possible to ascribe any specific reaction product to their decomposition.

Temperature Dependance and Arrhenius Parameters

As with the crystalline *cis*-R-THNA trimer, the An_2S trimer syrup was pyrolyzed for various times at four temperatures (280 °C, 263 °C, 240 °C, and 230 °C). A rate constant for AMNC formation was determined for each diastereomer pair at each temperature, as was done above at 230 °C. These data are plotted in Figure 6 as log k vs. 1/*T* in order to obtain the activation energies and the log A values shown in Table 1.

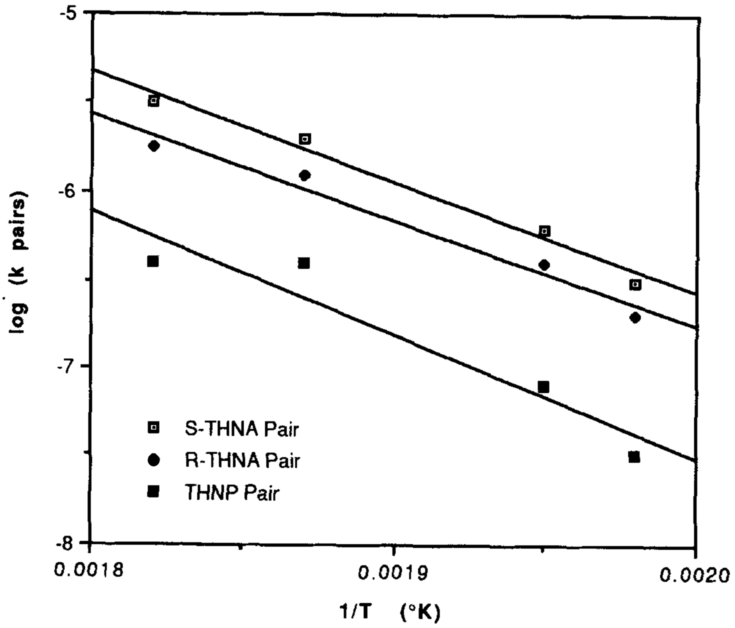


Figure 6 Arrhenius Plots for three *cis-trans* diastereomer pairs.

Several conclusions can be drawn from Figure 6 and the preceding data. As a general trend, the S-THNA pair decomposes from 50 % to 70 % faster than the R-THNA pair at each temperature tested. Likewise, the THNP pair is almost an order of magnitude slower than the faster S-THNA pair at each temperature. Neither the activation energies nor the log A terms of the three pathways are significantly different. However, the rate differences appear largely due to the entropy differences among the three routes (these are expressed in the log A values). The rate constants that are used for determination of the activation parameters very likely involve the rate constants for the equilibria that precede the decomposition. The low log A values may very well reflect one of these rate constants (e.g., the cyclization reaction).

CONCLUSIONS

- Ethylene is produced in the reaction, supporting the proposed retro-Diels-Alder mechanism for AMNC formation.
- Stereochemistry is quickly scrambled at the 4-position of each trimer; likely by tautomerization of the nitrile.

- Stereochemistry is slowly scrambled at the 1-position of each trimer; likely by a bond-cleavage/recombination mechanism. The buildup of propionitrile and 1-cyanonaphthalene in the pyrolysate support the cleavage/recombination mechanism.
- Decompositions are first order in trimer.
- The four THNA isomers decompose quickly, primarily to AMNC.
- The THNP isomers decompose slowly to unknown products.
- The reactions forming AMNC are autocatalytic, probably in AMNC.

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