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THERMAL DECOMPOSITION OF CYCLOADDUCTS OF VINYLNAPHTHALENES WITH ELECTRON-DEFICIENT DIENOPHILES

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The thermal polymerization of styrene is a long-known and well-practiced phenomena. While the mechanism of the thermal initiation event has been the subject of several investigations, it is not yet well understood. In an attempt to gain further insight as to the details of possible initiation from styrene dimer, analogous stable cycloadducts (maleic anhydride, tetracyanoethylene) of 1- and 2-vinylnaphthalene have been synthesized, fully characterized spectroscopically, and subjected to thermal decomposition. In the main, the major thermal event observed for these styrene dimer mimics is retro cycloaddition. This process is characterized by an activation enthalpy of approximately 30 kcal mol^{-1}. A minor process which accompanies the major reaction is the homolysis of a carbon–hydrogen bond to generate a carbon radical which may be trapped as a stable adduct of the 2,2,6,6-tetramethylpiperinyloxy (TEMPO) radical.

Keywords: *activation parameters, nitroxyl scavaging of radical intermediates, retro cycloaddition, styrene dimer, thermal initiation of styrene polymerization*

Introduction

The self-initiated (spontaneous) polymerization of styrene has received much attention over the past fifty years [1]. It was on this process that the commercialization of poly(styrene) was based. Yet a full understanding of how the polymerization is brought about has not been realized. The polymerization is known to be a radical process since inhibitors prevent the reaction and radical polymerization kinetic expressions correctly predict the outcome. It has been suggested that the initiation sequence involves a 4+2 cycloaddition reaction between two styrene molecules to form a dimer. The dimer is unstable and can react with a third styrene molecule by hydrogen atom transfer to generate two radicals capable of initiating styrene polymerization [2]. Because of its instability, reactions of the styrene dimer cannot be assessed directly. Therefore, stable cycloadducts which might serve as suitable styrene dimer mimics have been prepared and subjected to thermolysis.

Experimental

Materials

Cycloadducts of 1- and 2-vinylnaphthalene with both maleic anhydride and tetracyanoethylene were prepared.

1,2,3,$l0_a$-Tetrahydrophenathrene-1,2-dicarboxylic anhydride (THPA-1). A solution of 1-vinylnaphthalene (1.005 g, 0.0065 mole) and maleic anhydride (from Aldrich Chemical Company; 0.806 g, 0.0082 mole) in 15 mL of toluene was stirred under nitrogen at solvent reflux for 4 h. The solvent was removed by rotary evaporation to afford a white solid which was washed, by decantation, with several portions of methanol and collected by filtration at reduced pressure. The white solid was dissolved in hot glacial acetic acid to afford a solution from which crystals were deposited (0.827 g, 51.2% yield), 1,2,3,10_a-tetrahydrophenathrene-1,2-dicarboxylic anhydride, DSC mp 202 ([186–189°C] [3]): ^{1}H NMR (δ, $CDCl_3$), 2.10 (m, 1H, methylene proton), 2.80 (m, 1H, methylene proton), 3.43 (m, 1H, aliphatic proton), 3.59 (t, *J*=7.3 Hz, 1H, aliphatic proton,), 3.80 (dd, *J*=6.13 and 3.40 Hz, 1H, aliphatic proton,), and 6.15 (dd, *J*=3.16 and 6.74 Hz, 1H, olefinic proton), 6.82 (m, 1H, olefinic proton), 7.09–7.21 (m, 3H, aromatic protons), 7.72 (d, *J*=6.91 Hz, 1H, aromatic proton,); ^{13}C NMR (δ, DMSO) 26.1 (methylene carbon atom), 37.5 (aliphatic carbon atom), 39.1 (aliphatic carbon atom), 46.5 (aliphatic carbon atom), 120.7 (olefinic carbon atom), 122.6 (aromatic carbon atom), 127.2 (olefinic carbon atom), 129.5 (olefmic carbon atom), 128.5–129.0 (3 quaternary aromatic carbon atoms, 129.4 (quaternary carbon atoms), 131.3 (quaternary carbon atom), 135.9 (quaternary carbon atom), 173.2 (carbonyl carbon atom), 176.1 (carbonyl carbon atom); IR (cm^{-1}) 3081(w) (sp^2 C–H stretch), 3056(w) (sp^2 C–H stretch), 3030(w) (sp^2 C–H stretch), 2966(w) (sp^3 C–H stretch), 1847(s) and 1714(s) (C=O stretch); mass spectrum *m*/*e* (% of base) 76 (12%), 89 (14%), 152 (16%), 179 (100%), 224 (19%), 252 (13% M^+).

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Three other adducts: 3,10$_a$-dihydro-1,1,2,2-tetracyanophenanthrene (TCP-1), 2,3,4,10$_a$-tetrahydrophenanthrene-3,4-dicarboxylic anhydride (THPA-2) and 2,4$_a$-dihydro-3,3,4,4-tetracyanophenanthrene (TCP-2) were prepared and characterized using similar methods.

Methods

Instrumentation

Both starting materials (vinylnaphthalene cycloadducts with polar dienophiles) and thermolysis products were fully characterized by spectroscopic methods. Nuclear magnetic resonance spectra (NMR), both proton and carbon-13 were obtained using a General Electric QE-300 instrument, operating at 300 and 75 MHz, respectively, and dilute solutions in deuterochloroform or dimethyl sulfoxide-d$_6$. Tetramethylsilane (TMS) was used as an internal reference. Experiments required for the assignment of chemical shifts (COSY, DEPT, HETCOR, etc.) were carried out using GE software and appropriate parameters. Infrared spectra were recorded using solid solutions (1%) in anhydrous potassium bromide (KBr pellets) or neat liquids between sodium chloride plates and a PerkinElmer model 1600 FTIR instrument. Mass spectra were obtained using a Hewlett Packard model 5997 GC/MS with programmed temperature inlet or direct insertion as appropriate and an ionizing potential of 70 eV.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out using TA Instruments, Inc., model 2100 thermal analysis system equipped with a model 2910 DSC module and a model 2950 TGA unit. DSC curves were generated at a heating rate of 5°C min^{-1}. The cell was subject to a constant nitrogen purge at 50 mL min^{-1}.

HPLC

Thermally-induced decomposition of the adducts was observed for solid-state samples using thermogravimetry [4]. The kinetics of the retro cycloaddition reaction for each of the adducts was examined in inert solvent at several temperatures. In a typical experiment, a solution of adduct (0.040 molar) in chlorobenzene, bromobenzene, 1,3-dichlorobenzene, or 1,2,4-trichlorobenzene was brought to solvent reflux. After constant reflux had been fully established (usually 10 min after initial reflux was observed), aliquots of the mixture were periodically removed, rapidly transferred to a sample vial maintained at 0°C to quench the reaction, and analyzed by HPLC using a reverse phase (Whatman Partisil DOS-3) column with 70:30 acetonitrile/water at 1.5 mL min^{-1} as the mobile phase, and ultraviolet detection (311 nm). The progress of reaction was followed by monitoring the disappearance of the cycloadduct. In general, the change in concentration of the cycloadduct (as the HPLC peak area) as a function of time was used to determine rate constants. Activation parameters for the decomposition reactions were obtained using rate constants determined at several different temperatures.

Results and discussion

The 2+4 cycloadducts of 1- and 2-vinylnaphthalene with maleic anhydride (THPA-1 and THPA-2, respectively) and tetracyanoethylene (TCP-1 and TCP-2, respectively) have been synthesized, fully characterized and subjected to thermal degradation in both the solid-state and in solution. Thermogravimetry data suggest that each of the adducts decomposes thermally to generate the components from which it was formed, i.e., an initial mass loss corresponding to the fractional mass of the dienophile component in the cycloadduct was observed. This was confirmed by decomposition in solution (chlorobenzene, bromobenzene, 1,3-dichlorobenzene, or 1,2,4-trichlorobenzene as solvent). In this case the products of reaction were isolated and rigorously identified by spectroscopic methods. Rate constants were determined at several temperatures and are summarized in Table 1.

Table 1 Rate constants for the thermolysis of vinylnaphthalene cycloadducts

Adduct	Temperature of decomposition/°C	Rate constant/s$^{-1}\cdot 10^5$
THPA-1	156	1.45±0.07
	180	9.94±0.035
	214	104±1.4
THPA-2	156	0.006±0.008
	180	1.86±0.021
	214	64.2±0.021
TCP-1	180	7.86±0.02
	197	14.5±0.7
	214	246±3
TCP-2	156	1.60±0.028
	180	6.08±0.007
	214	63.0±2.5

Values reported reflect the averages of duplicate or multiple determinations and are accompanied by the average deviation in each case.

The activation enthalpy, $\Delta H^{\neq}$, for the decomposition of each adduct was determined from the slope of a plot of $\ln(k/T)$ *vs*. $(1/T)$ where k is the rate constant and T the Kelvin temperature. The activation entropy, $\Delta S^{\neq}$, at 298 K was then calculated using the expression

$$\Delta S^{\neq}/R=\ln k-23.760-\ln T+\Delta H^{\neq}/R$$

where k and T have the identities defined above, R is the gas constant, and the quantity 23.760 represents $\ln(k/h)$ where k is the Boltzmann constant and h is the Planck constant. The values for these parameters are displayed in Table 2. The values for $\Delta H^{\neq}$ are those that might be expected for a retro cycloaddition reaction, approximately 30 kcal mol^{-1} . In general, the values for $\Delta S^{\neq}$ are small negative – again suggestive of a unimolecular decomposition. An exception is the decomposition of TCP-1 for which $\Delta H^{\neq}$ is 42 kcal mol^{-1} (176 kJ mol^{-1}) and $\Delta S^{\neq}$ is 16.3 cal mol^{-1} K^{-1} (68.3 J mol^{-1} K^{-1}). The small positive value for $\Delta S^{\neq}$ may reflect the influence of solvent reorganization on formation of the activated complex.

Table 2 Activation parameters for the thermolysis of vinylnaphthalene cycloadducts

Adduct	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}_{289\ \mathrm{K}}$/cal mol^{-1} K^{-1}
THPA-1	29.66±0.44	–12.23±0.034
THPA-2	32.31±0.07	–7.02±0.16
TCP-1	42.3±0.12	16.3±1.3
TCP-2	25.54±0.12	–21.71±0.34

The uncertainties were obtained using the observed uncertainties for the rate constants and assuming a temperature uncertainty of ±1 K.

Chromatographic (HPLC) analysis of the product mixtures revealed the presence of no products other than those expected from the retro cycloaddition. This was somewhat surprising. If these adducts were to mimic the proposed behavior of the styrene dimer the formation of more fully aromatized products resulting from 1,3-hydrogen atom shift (presumably as a caged radical intermediate) might have been expected. Evidence that his reaction is present, albeit at a very low level compared to the major reaction, is provided by two observations. The first is that these adducts initiate styrene polymerization. The second is that decomposition of the adducts in the presence of the stable 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical affords the expected coupling product. The structure of the TEMPO adduct may be confirmed by X-ray crystallographic techniques and establishes unambiously the nature of the radical precursor.

Conclusions

Cycloadducts of 1- and 2-vinylnaphthalene with maleic anhydride and tetracyanoethylene undergo thermolysis to generate, in the main, the components from which they were derived. This is a typical unimolecular decomposition reaction with an activation enthalpy of about 30 kcal mol^{-1} and a small negative activation entropy. A minor pathway for decomposition of these adducts involves carbon-hydrogen bond homolysis to generate a radical intermediate which may be trapped with a stable nitroxyl radical.

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