

THE DIFFERENTIAL THERMAL ANALYSIS OF THE DIELS-ALDER REACTION  
OF CYCLOPENTADIENE

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Our previous investigation (1) of the cis-trans isomerization of cis-stilbene by differential thermal analysis (DTA) illustrated the feasibility of studying other types of thermally induced reactions by the same method. Therefore we undertook a study of the Diels-Alder reaction of cyclopentadiene. This reaction cannot be studied by conventional DTA methods because of the high vapor pressure and low boiling point of cyclopentadiene. We have found that if one seals the sample in the 4mm glass cells supplied with the duPont Model 900 Differential Thermal Analyzer calorimeter cell the system can withstand pressures up to forty-five atmospheres. Using this technique we have been able to determine simply and rapidly some kinetic parameters for the catalyzed and uncatalyzed dimerization of cyclopentadiene, the retrogression of endo-dicyclopentadiene, and the isomerization of endo-dicyclopentadiene to the isomeric exo form.

As is well known, extensive investigations of the Diels-Alder reaction have been carried out by conventional methods. A review of these reactions can be found in the recent book by Wassermann (2).

The reactions were followed by gas-liquid chromatography using a  $\beta$ , $\beta'$ -oxydipropionitrile column which has been shown by Hammond and Turro (3) to be effective in separating the endo and exo forms of dicyclopentadiene.

Figure 1 shows the typical thermogram obtained with freshly distilled cyclopentadiene. For ease of discussion the thermogram has been divided into regions A, B, C and D. We observed the conversion of cyclopentadiene to endo-dicyclopentadiene in Region A. The activation energy for this reaction was determined by the method of Piloyan et al (4).

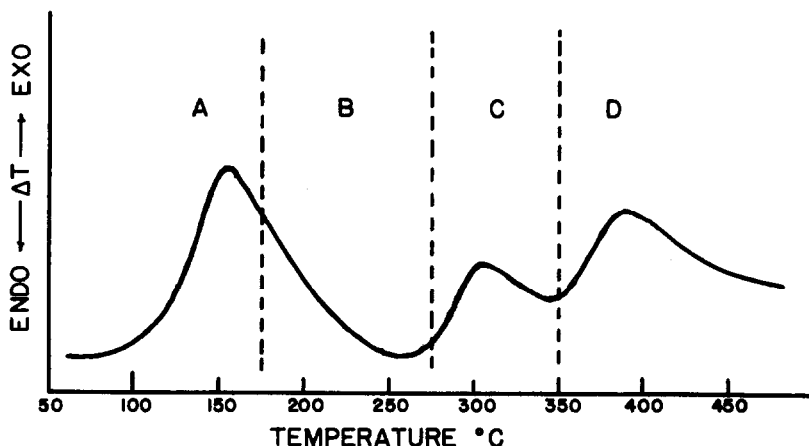


FIG. I  
Cyclopentadiene

Region B corresponds to the retrogression of the initially formed endo-dicyclopentadiene as shown by the increased monomer concentration appearing in this region. Further evidence for this reversal is found when one examines Figure II, the thermogram of pure endo-dicyclopentadiene; the endotherm expected for the cracking of the endo-dicyclopentadiene is clearly evident in the region. The activation energy for this reverse Diels-Alder reaction may be estimated from the initial portion of the endotherm in Figure II. Our value of 36.1 Kcal/mole again agrees with the value of 35.3 ± 0.6 Kcal/mole reported by Khambata and Wassermann (7). Furthermore, while maleic anhydride reacts instantaneously with cyclopentadiene at room temperature, reaction with dicyclopentadiene occurs only in the temperature range in which cracking occurs. Figure III shows the exotherm corresponding to this reaction.

In Region C of Figure I the exotherm corresponds at least in part to the conversion of endo to exo-dicyclopentadiene as evidenced by the appearance of a new peak in the vapor phase chromatogram whose retention time (8) and

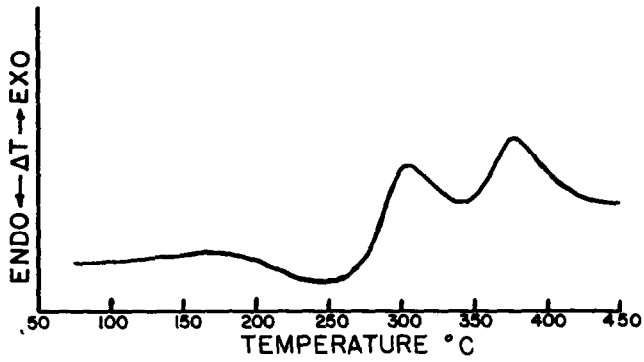


FIG. II  
Endo-Dicyclopentadiene

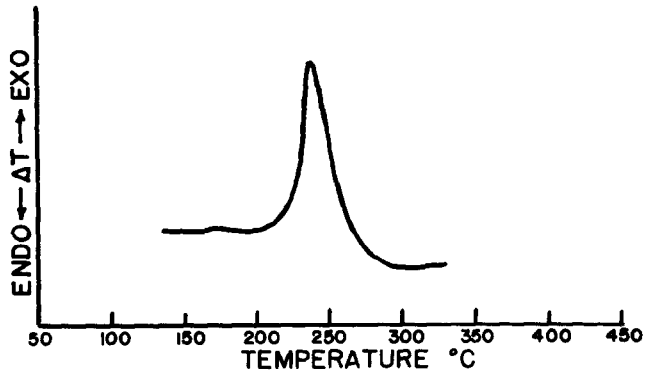


FIG. III  
Endo-Dicyclopentadiene and Maleic Anhydride

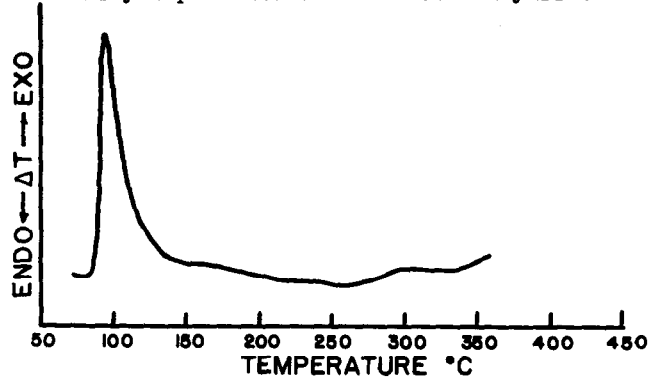


FIG. IV  
Cyclopentadiene and Hydrogen Chloride

infra-red spectra (9) correspond to those of the exo isomer. There is evidence however, that in addition to the isomerization there is formation of some polymeric Diels-Alder products.

Region D. was not fully characterized but the appearance of the sample indicated polymerization and some decomposition.

We have examined and confirmed the HCL catalyzed dimerization of cyclopentadiene (10). Figure IV shows a typical thermogram of cyclopentadiene saturated with HCL. The exotherm which corresponds to the formation of endodicyclopentadiene now occurs 60° lower than the uncatalyzed sample.

We feel that with this modification many thermally induced reactions which formerly could not be investigated will now be susceptible to analysis.

#### Acknowledgement

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