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A STUDY OF THE OLEIC-ELAIDIC ACID ISOMERIZATION BY DIFFERENTIAL THERMAL ANALYSIS

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We have previously investigated the heterogeneous catalysis of the isomerization of cis-stilbene by differential thermal analysis (DTA)(1). We now report the study of the homogeneous catalysis of the cis-trans isomerization process. Since the homogeneous selenium catalyzed conversion of the naturally occurring fatty acid, oleic acid, to its isomer, elaidic acid, has been thoroughly studied(2), we have chosen it as our model system. In addition, we wish to report that the homogeneous conversion catalyzed by iodine can be studied by DTA for both thermal and photochemical processes. To our knowledge this is the first attempt to study a photochemical process by DTA.

The problem of volatility at high temperature which has prevented previous studies of this type using conventional and commercially available instruments can be successfully handled by using sealed glass cells(1,3,4). We have found that the 4mm pyrex cells available for the duPont model 900 DTA macro cell are particularly effective. When sealed they have withstood pressures in excess of forty five atmospheres and have eliminated the base line problems associated with vaporization and boiling.

The thermal conversion of oleic to elaidic acid is shown in the thermogram of figure 1-A. That this thermogram corresponds to isomerization of the oleic acid was verified by infrared analysis(5) of samples taken at various stages along the exotherm. The method of Piloyan et al(6), which can be used to calculate activation energies from thermograms, could not be applied to this particular thermal process because of the visually observed simultaneous decomposition accompanying the isomerization. The heterogeneous catalysts, 10% palladium on charcoal and 10% platinum on charcoal, which are effective as catalysts for the cis-stilbene system, are ineffective in the oleic acid case, giving virtually the same thermogram as the thermal process shown in figure 1-A.

Figure 1-B shows the thermogram for the homogeneous, selenium-catalyzed isomerization

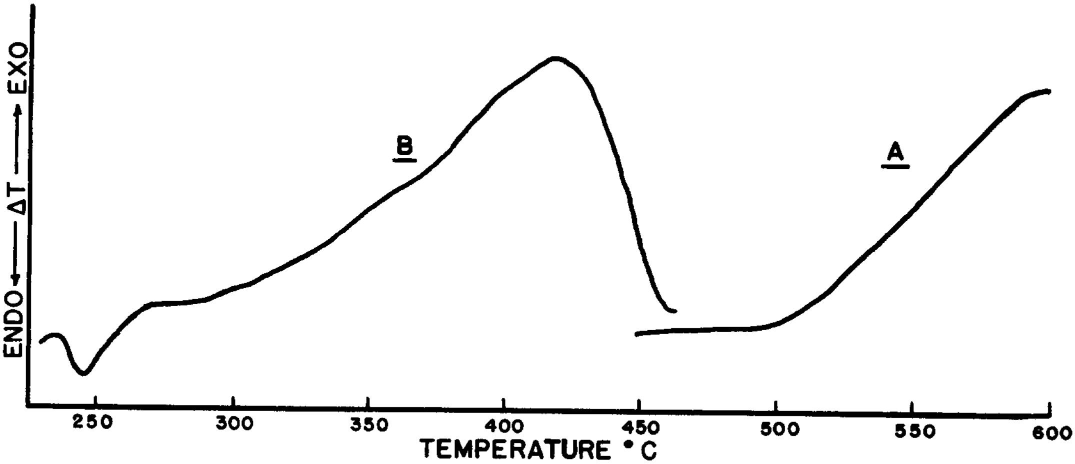

FIG. 1

A- Thermogram of pure oleic acid

B- Thermogram of oleic acid containing 0.2% selenium

of oleic acid. The exotherm, peaking at approximately 420° represents the isomerization and yields an activation energy of 31 ± 3 kcal/mole in good agreement with the value of 30 kcal/mole reported by Orchin(2).

The thermogram for the isomerization in the presence of I_2 is shown in figure 2-C. The reaction occurs at a much lower temperature, peaking at about 355°C with an activation energy of 32.5 ± 0.5 kcal/mole. Such cis-trans isomerization catalysis by thermally generated iodine atoms has been extensively studied for many cis olefins(7,8,9).

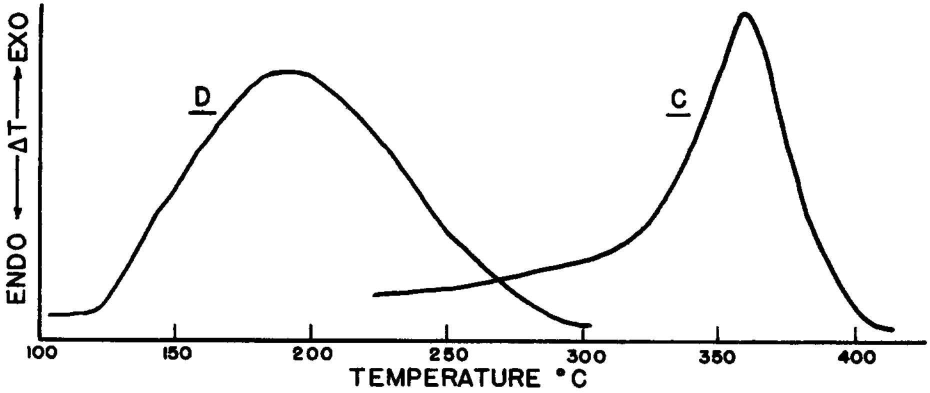

FIG. 2

C- Thermogram of oleic acid containing a trace of iodine

D- Thermogram of oleic acid containing a trace of iodine and exposed to visible radiation from a tungsten lamp

In order to study catalysis by photochemically generated iodine atoms the DTA cell was modified in the following manner. The metal cap for the thermal chamber was replaced with a pyrex glass plate. The standard glass bell jar was then placed over the system. A heat filtered tungsten lamp was focused at the heating chamber from above the bell jar. The thermogram obtained showed a large decrease in activation energy as can be seen in figure 2-D. The exotherm peaked at about 185°C and corresponded to an activation energy of 20.4 ± 0.3 kcal/mole. It should be noted that in the absence of visible light no isomerization occurs in the region of 185°C (see figure 2-C). The difference in activation energies for the thermal and photochemical processes is 12 kcal/mole. It has been postulated(10,11) that a value equal to one half the bond dissociation energy of the iodine molecule ($\Delta H\ I_2 = 36$ kcal/mole) would be consistent with catalysis caused by iodine atoms.

During the course of this investigation, it was observed that solutions of iodine in oleic acid which were preheated to 225°C for approximately thirty seconds, allowed to cool and then analyzed by DTA while being irradiated with the tungsten lamp, showed only thermal catalysis. This suggests that molecular iodine and oleic acid form a complex which only undergoes a thermally induced isomerization. The fact that the value of 12 kcal/mole which we obtained is smaller than half the bond dissociation energy of the iodine molecule would be consistent with the prior formation of such a complex. This problem is now under active investigation.

Acknowledgement

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