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# ACCELERATION OF A DIELS-ALDER REACTION IN AN ULTRACENTRIFUGE

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**Summary:** The reaction rate for the Diels-Alder reaction between maleic anhydride and furan is increased when performed in an ultracentrifuge.

It is well known that many reactions can be accelerated by the application of high pressure[1]. This can be particularly advantageous when the products are heat sensitive[2]. The pressure at the bottom of a liquid column is not only a function of its height and density, but also of the gravitational force. Ultracentrifugation produces extremely high centrifugal forces (over 400,000g). Thus, by using a 60 mm column placed in an ultracentrifuge equipped with a 400,000g rotor, the pressure will range from 1 bar at the top of the column to approximately 2 kbar at the bottom. In this work we report the effect of centrifugation on the Diels-Alder reaction between maleic anhydride and furan.

Furan (1.70 g, 12.7 mmol) was added to a solution of maleic anhydride (1.25 g, 12.7 mmol) in dry acetone (25 ml). Part of this solution was reacted at room temperature and atmospheric pressure (RTP experiment) while part was loaded into tubes and reacted in a Beckman L5-65 Ultracentrifuge, utilizing a SW60Ti swinging bucket rotor (height of liquid column 60 mm). The tubes were centrifuged at 55,000 rpm (400,000g) for 23 hours at 20 to 23 °C. The ambient temperature ranged from 20 to 25 °C. The centrifuge was allowed to brake slowly, and the tubes were carefully handled to prevent mixing of their contents. Samples were withdrawn from the top **T**, middle **M**, and bottom **B** of one tube, while the contents of another tube **X** were mixed before sampling. A sample **R** was also taken from the RTP experiment. For all the samples the solvent and excess furan were evaporated at reduced pressure. The residue after evaporation was dissolved in acetone-$d_6$ and the ratio of 7-oxabicyclo(2.2.1)hept-5-ene adduct **(H)** to maleic anhydride **(MA)** was measured by NMR (Varian XL-300). The results are as follows:

| Sample | Ratio ((H):(MA)) | Sample | Ratio ((H):(MA)) |
|---|---|---|---|
| **T** | 0.63 | **R** | 0.68 |
| **M** | 1.06 | **X** | 1.14 |
| **B** | 1.46 | | |

It was noticed that the amount of material in the three samples increased in the order **T**, **M** and **B**. Therefore, a reference run was performed in which acetone solutions of furan (10 %), maleic anhydride **(MA)** (10 %) and a **(MA)**/**(H)** mixture (2:1, 5 %) were centrifuged. Their rates of sedimentation were found to be the same within ± 5 %. Thus, the differences in the rates of formation of the Diels-Alder product **(H)** found cannot be explained on the basis of differential sedimentation. It should be noted that the rate of formation of **(H)** in sample **T** is slightly less than that in sample **R**. This is probably due to the fact that the ultracentrifuge experiment was conducted at a slightly lower temperature than the RTP experiment.

Another experiment was performed in which ethyl acrylate was reacted with furan in various solvents: neat furan, ethanol and chloroform/ethanol (1:1). Since pressure is a function of liquid density, an increase in reaction rate with increased density of the solvent was expected. An increase in the reaction rate was demonstrated, but the sluggishness of the reaction (only 1.5 % completed in 24 hours) and the difficulty in comparing reaction rates in different solvents give this observation only a qualitative value. (Maleic anhydride could not be used in this experiment because of its insolubility in chloroform.)

In conclusion, an increase in the rate of the Diels-Alder reaction as a function of the centrifugal pressure was observed. This suggests that the utilisation of an ultracentrifuge for kinetic studies might be advantageous, as multiple pressures can be studied simultaneously. Differences in the rates of sedimentation, which serendipitously were unimportant in this case, have to be carefully watched.

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