Tetrahedron Letters, Vol. 34, No. 32, pp. 5039-5042, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Thermal Decomposition of Dimethyldioxirane

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Abstract: The thermal decomposition of dimethyldioxirane (DMDO) was followed by uv/vis spectroscopy at 340 nm. At high concentration of DMDO (~0.1M) the decomposition was found to to have an induction period followed by rapid decay. The rapid decay was shown to be caused by presence of reaction products. At low concentration of DMDO (~0.02M) the decomposition was found to be first order with an Ea of 24.9 kcal/mol. Based on this result it is estimated that the dioxybiradical produced by cleavage of the O—O bond shows an activation energy of about 10 kcal/m for reclosure back to the DMDO.

There has been a great deal of research involving the chemistry of dimethyldioxirane since its synthesis and isolation.[1] However, previous research has been primarily concerned with the reactivity of this highly strained system with a myriad of substrates.[2] For instance, there have been studies done on the DMDO reactivity with triphenylphosphine, cis-stilbene,[1] silylenol ether.[3] Less work has been done on the thermochemistry of the system. There are a number of theoretical calculations on the CH_2O_2 energy surface. The lack of experimental data on DMDO is a result of reports in the literature that the decomposition kinetics of DMDO were not first order but that it "exhibits a pronounced inhibition period followed by rapid decay." and that the half-life at room temperature of DMDO was about seven hours.[4] We wish to report that at low concentrations the decomposition of DMDO is a simple first order decay.

RESULTS AND DISCUSSION

Dimethyldioxirane was synthesized according to the procedure used by Adam (reaction of acetone and potassium monoperoxy sulfate [oxone] in the presence of sodium bicarbonate).[4] Once the pale-yellow solution was collected in the receiving vessel (no attempt was made to dry the solution), we used several methods to confirm that the solution was really DMDO in acetone. First, a uv/vis absorption spectrum was taken and the max. absorbance at 335 nm was in accord with previous reports. The concentration of DMDO was determined using the absorbance and the extinction coefficient (ε =10) reported by Adam. Second, an H-NMR was taken in deuteroacetone and we observed a peak at 1.65 ppm which is also in agreement with previous reports. Third, we treated the DMDO-acetone solution with cyclohexene and we observed the same epoxide, cyclohexene oxide, that was produced when we reacted m-chloroperbenzoic acid and cyclohexene (products were confirmed using GC/MS and H-NMR).[5]

We studied the thermal decomposition of DMDO by following its decay by uv/vis at 340 nm. Several experiments were run at room temperature (about 23°C) at the concentrations of DMDO as initially isolated by

distillation (ca.0.09-0.16M). We observed the same phenomenon reported in the literature, namely slow decay followed by a rapid decomposition.[6]

We varied the temperature and observed the same phenomenon. However, the observed behavior occurred at an earlier time during the high temperature runs than those that were done at low temperature. Murray had heated the DMDO and observed the formation of acetone peroxide dimers and trimers and later reported methyl acetate and other esters.[7] They hypothesized a radical chain reaction. It seemed clear that some of the rapid decay was due to self catalyzed decomposition. We hypothesized, that the cause of the rapid decay might be the result of the catalytic effect of the build up of products on the decomposition of the DMDO. To test this hypothesis we did several experiments. We ran the thermal decomposition at lower initial concentrations of DMDO and we ran the decomposition in the presence of products from the outset of the reaction. The results of those experiments are shown in Figure 1.

The three plots are all decompositions of DMDO followed at 340 nm at 50°C. The 0.12 M DMDO plot is typical of the results of all the thermal decompositions run at high concentrations (above about 0.02 M). It displays the rapid decay after an induction period as reported in the literature. The decomposition done at 0.02 M shows a simple first order decay. The last plot is that of a 0.02 M decomposition where the diluent solution was the solution remaining from the 0.12 M decomposition. This decomposition of the DMDO is done, from the outset, in the presence of products. It shows no induction period prior to nonlinear behavior and also showed accelerated decomposition over the other low concentration run.[8]

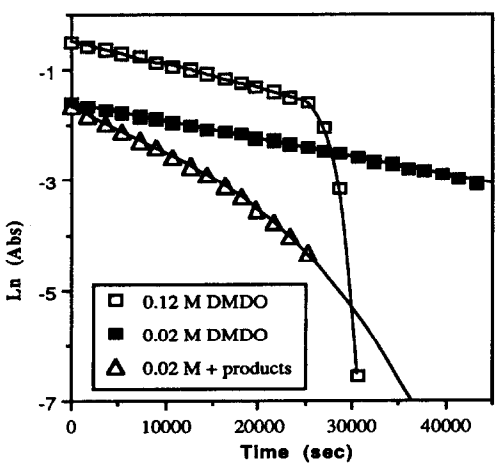


FIGURE 1. Plots of Ln(Abs) at 340 vs. time at 50°C for the three solutions of DMDO as described in the text.

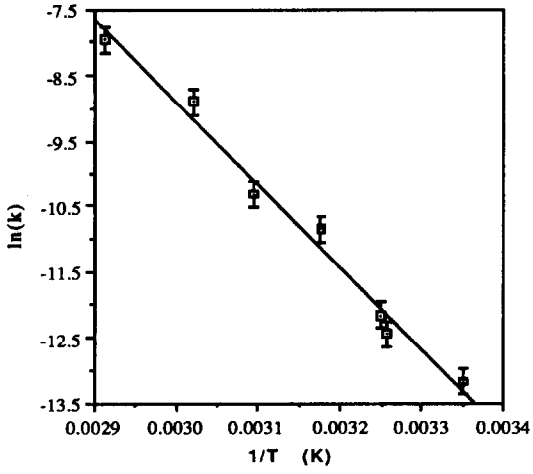
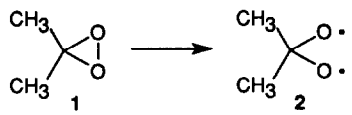


FIGURE 2. Arrhenius plot of the kinetic data for the first order decomposition of DMDO.

Since the DMDO thermal decomposition is first order if the reaction is run at low enough concentration, it is possible to study its first order thermal decomposition as a function of temperature. This was done at an initial DMDO concentration of 0.02 M over the temperature range 25° - 75°C and the decay was found to be first order. An Arrhenius plot (Figure 2) of the data gives an activation energy (Ea) of 24.9 kcal/m with a rate



constant at 25°C of 1.53 x 10^{-6} sec^{-1} ($t_{1/2}$= 5.2 days). The Ea does not agree with a previous estimate by Adam, et. al. of 15-16 kcal/m.[2]

Estimates of the activation energy, Ea(**1**,**2**) for the above reaction can be gotten by considering the thermochemistry of the bonds involved in the reaction and the activation energy of the reverse reaction, Ea(**2**,**1**). Adam, et. al.'s thermochemical estimate was based on an estimated <1 kcal/m activation energy, Ea(**2**,**1**) for the reclosure of diradical **2** and the estimates of $\Delta H°(\mathbf{1},\mathbf{2})$ from work on the CH_2O_2 system. A number of theoretical calculations on the CH_2O_2 system gave estimates for the $\Delta H°$ for ring opening of **1** to **2** of about 15 kcal/m. The sum,

$$Ea(\mathbf{1},\mathbf{2}) = \Delta H°(\mathbf{1},\mathbf{2}) + Ea(\mathbf{2},\mathbf{1}), \quad (1)$$

is the activation energy, Ea(**1**,**2**) for the forward reaction. Our experimental result of 24.9 kcal/m indicates a slightly more complex picture.

The difference between our result and Adam's estimate probably results from his underestimation of the activation energy of the reverse reaction, Ea(**2**,**1**). While normal radical-radical recombination reactions have very small activation energies it is likely that the recyclization of species **2** will have a higher activation energy. The formation of the cyclic **1** results in about 27.6 kcal/m of strain energy due to the formation of the three membered ring. Some of that energy must be present in the transition state for reclosure. In fact the difference between our activation energy for **1** to **2** of about 25 kcal/m and $\Delta H°(\mathbf{1},\mathbf{2})$ of 15 kcal/m gives an estimate of that number of about 10 kcal/m. About a third of the total strain energy of the three membered ring is present in the transition state for reclosure of the biradical. Ironically the apparent thermal stability of DMDO is due to the very strain energy that would, at first seem to make the species so unstable.

ACKNOWLEDGEMENTS

We wish to thank the New York University Faculty Resource Network for sabbatical support and the Union College Summer Student Fellowship Program.

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4. Adam, W.; Chan, Y.; Cremer, D.; Gauss, J.; Scheutzow, D. C.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800-2803.
5. H-NMR's were recorded on a Gemini 200 (Varian). Samples were measured in acetone, and deuterated acetone and deuterated chloroform. UV spectra were obtained on a Hewlett Packard 8452A Diode Array Spectrophotometer with a 1 cm quartz cell. GC/MS were obtained on a Hewlett Packard 5890 Series II and Hewlett Packard 5971A Mass Selective Detector. Temperatures were measured using an Omega 871 digital thermometer.
6. Three methods were used to study the thermal decomposition of DMDO. In the first method the DMDO solution is prepared by diluting it to the appropriate initial concentration with acetone and then transferring it to a spectrophotometric cell that sits in a thermally jacketed for the entire period of the experiment. For the second method the DMDO solution is prepared and then placed in a cell, but the cell is transfer back and forth from the cell jacket to a water-bath. The third method (for all runs above 50°C) requires the use

of 4 mL thick-walled vials. Once the DMDO solution is prepared, it is placed in a series of 4 mL thick-walled vials and then the vials are placed in the water-bath. At calculated time intervals, a vial is taken out of the water-bath and cooled rapidly in an ice-bath. The DMDO solution is then transferred to a cell and its absorbance is measured.

7. Singh, M.; Murray, R. W. *J. Org. Chem.* **1992**, *57*, 4263-4270.
8. To a spectrophotometric cell containing 0.5 mL (0.12 M) DMDO solution, 2.5 ml of the product solution from a 50°C thermal decomposition experiment was added. The cell was then placed in the cell jacket (kept at 50°C) of the spectrophotometer and its absorbance was measured as a function of time.

(Received in USA 3 May 1993; accepted 28 May 1993)