

A Mechanistic Model for the Uncatalyzed Reaction of Stilbene with H₂

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Keywords: Hydrogenation, Kinetics, ACUCHEM, Glass Catalysis

INTRODUCTION

During the past few years, we have studied the thermolysis of a number of different substrates in the presence of H₂ or D₂ as models for the hydrothermolysis of coal.¹ To avoid catalysis by metal surfaces our reactions are carried out in glass reaction vessels with a length of capillary tubing separating the reaction mixture from the steel containment chamber. In our initial study of the hydrothermolysis of diphenylethane (DPE) we noted that the concentration of stilbene (STB), diphenylethene, formed in this reaction goes through a maximum value as the reaction proceeds.^{1f} It was also noted that reactions carried out with lower starting concentrations of DPE generated less STB during the course of the reaction. There were few,² if any, examples of the uncatalyzed reactions of alkenes with H₂ in the literature, so we undertook to study the viability of such processes with selected substrates. Our initial survey used STB, 1-methylstyrene (2-phenylpropene), anthracene and phenanthrene.^{1a} We found that the first three compounds could be hydrogenated at 410 °C and 14 MPa of D₂. In the case of STB, we observed an inverse concentration effect in that the yield of DPE was greater with lower starting STB concentrations under otherwise identical conditions. The reverse seemed to be true for 1-methylstyrene. Anthracene was hydrogenated with no significant concentration effect and phenanthrene refused to give hydrogenation products under conditions which were effective for the other three compounds. Of the two compounds that showed unusual concentration effects, STB seemed the best behaved in that it gave mainly DPE as a reaction product, whereas 1-methylstyrene gave higher molecular weight byproducts. For this reason and because of its relevance to our earlier study of the hydrothermolysis of DPE, STB was chosen for a more detailed investigation of its kinetic behavior.

EXPERIMENTAL

Substrate. The best grades of commercially available *trans*-stilbene (*trans*-STB) contained small amounts of diphenylethane (ca. 0.7 %). Some runs were carried out with STB synthesized by a modified Wittig procedure.³ No significant differences were observed for reactions carried out with this pure substrate. Diphenylethane was recrystallized commercial samples and showed no gas chromatographically detectable impurities. *cis*-STB for preparation of GC/MS standard was a commercially available product.

Reaction Procedure. The reaction vessel and general procedure for hydrogenations has been described previously.^{1a} For the experiments described in this paper, greater attention was given to control of reaction temperature. Figure I shows differences in the temperatures registered by thermocouples placed (1) in the fluidized sandbath, (2) inside the glass reaction vessel and (3) between the glass vessel and its steel container. It will be noted that both internal temperatures lag behind that of the sandbath and remain substantially below it for a period in excess of ten minutes. The temperature inside and outside of the glass reactor become equal roughly four minutes after the reactor assembly is placed in the bath. These relationships varied somewhat depending on the particular steel reaction container employed, conditions in the sandbath, the shaking rate for the reactor, the depth of immersion of the reactor assembly, etc. As a result it was very difficult to reproduce exactly the reaction temperature from run to run as evidenced by variations in yield for reactions carried out for nominally equal times and temperatures. To avoid these problems, we adopted the approach of placing a small sealed capillary ampule containing DPE between the glass vessel and its steel housing. The arrangement is shown in Figure II. We then used the degree of thermolysis of DPE within this ampule to calculate an effective reaction time based on a separately-determined rate constant for the thermolysis of DPE placed in similar ampules emersed directly in the sandbath at 405 °C. The plot for DPE conversion is shown in Figure III. In essence, if 20% of DPE had been converted to products in the ampule, we read the effective time at 405 °C from Figure III (corresponds to approximately 150 min at 405 °C). This calculated time was then substituted for the

actually measured reaction time for the purpose of kinetic plotting of the STB conversion data.

Analysis of Reaction Mixture. *trans*-STB was converted to an equilibrium mixture of *cis*- and *trans*-isomers at temperatures well below that required for hydrogenation. Thus the product mixture consisted of an equilibrium mixture of *cis*- and *trans*-STB, DPE and, at longer times, products of the thermolysis of reduction-generated DPE. Unfortunately, the retention time of *cis*-stilbene was almost identical to that of DPE requiring that a secondary analysis of the gc peak by gas chromatography/mass spectrometry (GC/MS) be performed. Figure IV shows a plot of composition versus ion intensity ratios for synthetic mixtures of *cis*-STB and DPE integrated over the entire GC peak. This standard curve was used to calculate compositions of reaction mixtures.

Calculation of Theoretical Kinetic Plots. The ACUCHEM⁴ program was used to calculate theoretical curves of composition vs. time based on assumed rate constants as listed below.

RESULTS AND DISCUSSION

Although our earlier work attempted in several instances^{14, 15} to follow the progress of hydrothermolysis reactions as a function of time, great difficulty was encountered in reproducing reaction temperatures with sufficient precision to provide data suitable for kinetic analysis. To circumnavigate this uncertainty we arranged to carry out a second, monitoring reaction inside the metal housing, but outside of the glass reactor. A small sample of DPE was sealed in a glass capillary tube and inserted in the reactor as shown in Figure II. The progress of this secondary reaction served as an internal clock by which we could determine an "effective" time for the reaction at 405 °C. Composition of the reaction mixture vs. effective time at 405 °C is given in Table I for a runs carried out with 50 mg starting DPE. It is clear from perusal of this data that we have not eliminated as much scatter as we might have wished but a reasonable relationship between effective time and conversion may be adduced. Moreover, it is clear that we are far from the sort of pseudo first-order kinetics which might be expected for any simple bimolecular reaction between STB and H₂.

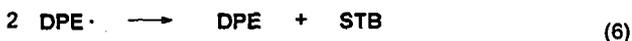
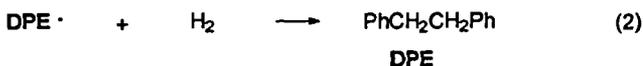
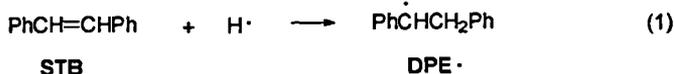
Table I. Composition of Reaction Mixtures for *trans*-STB with H₂ at 14 MPa vs. Effective Time at 405 °C.

Effective Time at 405 °C (min)	Reaction Composition					
	<i>t</i> -STB	<i>c</i> -STB	DPE	PhMe	PhEt	PhH
35.4	75.9	7.2	12.1	0.5	0.4	0.3
42.4	79.4	7.5	11.1	0.1	<0.2	<0.2
42.7	80.4	7.6	9.6	0.2	<0.1	<0.1
90.4	59.9	5.7	28.7	0.9	0.2	0.1
121	61.5	5.8	30.1	0.8	<0.4	<0.4
147	57.7	5.4	33.3	0.5	0.1	<0.1
214	26.2	2.5	60.4	4.6	1.3	0.6
264	18.4	1.8	62.7	7.3	2.0	1.1
388	0.6	<0.6	63.2	14.5	8.4	5.6

A log plot for disappearance of STB is shown in Figure V. The solid points represent experimental data with 50 mg and with 20 mg STB in the reaction bulb. Runs carried out with larger starting weights gave unmanageably slow conversion under these conditions.

The mechanistic model suggested earlier for this process¹⁴ consists most essentially of a kinetic chain process with H atoms and 1,2-diphenylethyl radicals, DPE[•], as chain carriers, eqs 1 and 2. The sequence generates DPE which can be expected to undergo its well-characterized dissociation to benzyl radicals, eq 3, followed by reaction of these both with H₂ and with DPE, eq 4 and eq 5, each process generating a chain carrier for the propagation cycle. The termination of the chain seems likely to be disproportionation of two DPE[•] to give DPE and STB, eq 6. There are a number of other processes known to be involved in the hydrothermolysis of DPE which might be considered, for example, the rearrangement of DPE[•] to give 1,1-diphenylethyl radicals. However, these would react to regenerate radicals and should not alter the kinetic pattern. Also, earlier work has shown that

the presence of H atoms can also lead to hydrocracking products, PhH and PhEt.¹⁷ However, Table I suggests that such processes become important only after the majority of the STB has been converted. This might be expected, as STB should be an effective trap for H atoms via eq 1.



Thus, a reasonable match of the kinetic data might be expected using only the sequence of eqs 1 through 6. It will be observed, however, that unless DPE is present initially, there is no initiation step for the chain. We found that commercially available STB invariably contained small amounts of DPE. Therefore, we went to some effort to synthesize DPE-free STB for selected experiments. As there was no significant difference in the kinetic data for these samples, we must assume that some other initiating process is involved. Temporarily avoiding the problem by arbitrarily imposing an unspecified process to generate H atoms from H₂ (with a rate constant, $k = 1 \times 10^{-7} \text{ s}^{-1}$) leads to the calculated plot in Figure V. The other rate constants used in its generation were as follows:

$k_1 = 5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Calculated from Benson's expression for the reaction of H· with ethylene.⁷)

$k_4 = 50 \text{ M}^{-1} \text{ s}^{-1}$ (This value is suggested by McMillen, Malhotra and Nigenda⁸ at 400 °C.)

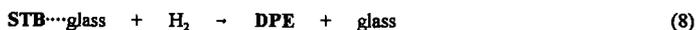
$k_2 = 9.3 \text{ M}^{-1} \text{ s}^{-1}$ (There was no guidance for this number but it could reasonably be expected to be somewhat smaller than k_4)

$k_3 = 2.4 \times 10^5 \text{ s}^{-1}$ (This is the first order rate constant from Figure III. It is in good agreement with literature values.⁷)

$k_5 = 1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (Calculated from the expression $\log k = 8.8 - 14.2/\phi$ (per hydrogen) estimated by Poutsma.⁹)

$k_6 = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Suggested by Poutsma⁸ to be $\log k = 8.5$, based on studies by various groups of the rate constant for disproportionation of 1-phenylethyl radical to give styrene and ethylbenzene.⁹)

Of course it is thermochemically unreasonable to assume that H₂ dissociates with a rate constant as large as 10⁻⁷. It is apparent that initiation occurs via some unknown catalytic process. As recent information indicates that silica can serve as a catalyst for the hydrogenation of alkenes,¹⁸ it seemed worth considering that the surface of the glass container was serving as a catalyst. Based on an estimate of the concentration equivalent of catalytic sites in our glass reactor being 3.2×10^{-11} , and the following reaction sequence, eqs 7 and 8 (with $k_7 = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_8 = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$):



the theoretical curves in Figure VI were calculated. While the match to experimental data is not as good as that of Figure V, the pattern and concentration dependence are preserved.

CONCLUSIONS

The scheme presented explains the inverse concentration effect noted earlier. At high concentrations of STB, the chain-carrying DPE· undergoes disproportionation, terminating the chain.

At lower concentrations, they stand a better chance of reacting with H₂. The rate increase with conversion is mainly due to the generation of DPE which serves as an initiator. We believe that this scheme is a reasonable mechanism for the hydrogenation of alkenes in the absence of metal catalysts, provided that some radical-generating initiator is present. We have also found that the hydrogen-transfer rate constants used in this scheme can be incorporated in a calculation to predict the pattern of D incorporation when DPE undergoes thermolysis under D₂.^{1f} The proposed initiation by glass surface in the absence of a radical-generating species is, at present, purely speculative.

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Figure I. Temperature Profile for Glass Reactor and Containment Vessel

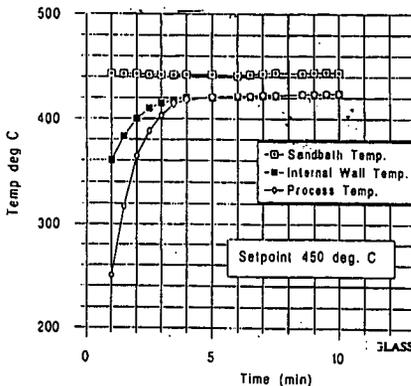


Figure II. Reactor Setup for Kinetics Experiments

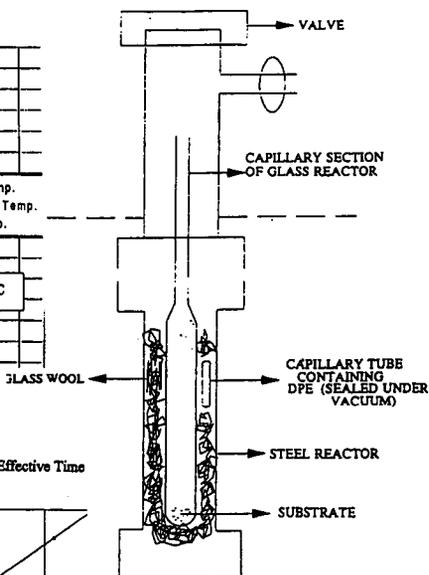


Figure III. Plot of DPE Loss Used for Calculation of Effective Time

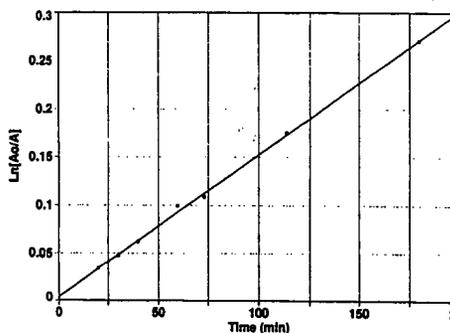


Figure IV. Calibration Curve Used to Determine DPE in the Presence of cis-STB

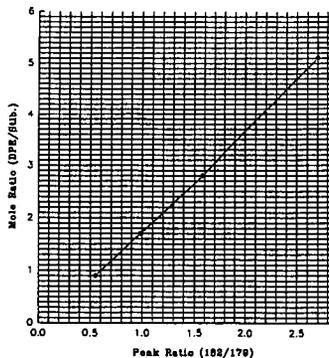


Figure V. Theoretical Matching of STB Loss (Unspecified H Atom Production)

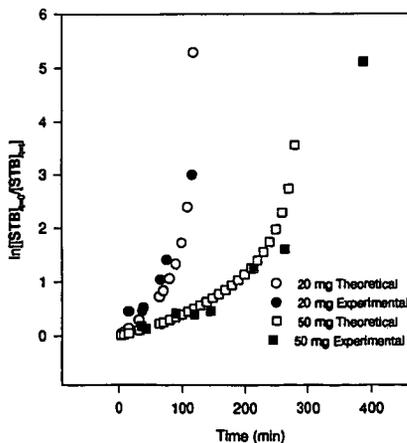


Figure VI. Theoretical Matching of STB Loss (Catalysis by Glass Reactor)

