

MASTER

THE ROLE OF THE HYDROGEN-DONOR
SOLVENT IN COAL HYDROLIQUEFACTION

Progress Report
for Period September 1, 1979 - November 30, 1980

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PERCENTAGE OF EFFORT AND COMPLIANCE WITH CONTRACT REQUIREMENTS

The principal investigator has devoted approximately 33% of full time effort to this project during the September, 1979 - May, 1980 school year, in addition to carrying 95% of a full teaching load. During the summer of 1980, the principal investigator is devoting 100% of full time effort to the research, and it is anticipated that he will devote approximately 33% of full time effort to the project during the period September 1 - November 30, 1980.

To the knowledge of the principal investigator, all contract requirements have been complied with from the beginning of the project to the present time.

A B S T R A C T

The principal disproportionation products of 1,2-dihydronaphthalene (1,2-DHN) are naphthalene (Nap) and tetralin (Tet). Dimers of 1,2-DHN constitute 17% and 5% of the respective liquid phase (285-315°C) and gas phase (385-410°C) products. The Nap:Tet ratio is one in the presence of solvents, but is >1 and <2 in their absence.

Gas phase reaction kinetics indicate that 1,2-DHN disappears by simultaneous first and second order reactions. These results are consistent with a concerted second order disappearance of 1,2-DHN to produce equal amounts of Nap and Tet, accompanied by either carbonium ion or free radical side reactions that produce more Nap than Tet, together with 1,2-DHN dimers. Preliminary evaluation of the liquid phase kinetics suggest they follow a similar pattern. The structures of the dimers should reveal whether they were formed by a carbonium ion or free radical mechanism. Isolation of the dimers will be attempted by preparative GC (PGC) followed by TLC to remove thermal decomposition products formed during PGC.

Exploratory results suggest that heating 1,2-DHN (300°C) in the presence of tetraphenylethane, which dissociates into diphenylmethyl radicals, may constitute a model for the free radical conversion of 1,2-DHN into Nap during coal hydroliquefaction. Further studies of this system will be conducted.

I N T R O D U C T I O N

Tetrahydroaromatic donor solvents such as tetralin (Tet) are converted into dihydro intermediates and then to fully aromatic compounds during the course of coal hydroliquefaction. The dihydro intermediates, in the absence of coal, are known to thermally disproportionate into tetrahydro and aromatic compounds (intrasolvent hydrogen transfer). Thus, in the process of coal hydroliquefaction, the dihydroaromatic solvent intermediates are apparently converted into aromatic compounds concurrently by two routes, reaction with coal, and disproportionation.

The objectives of this research project are:

- I. To determine the nature of the intrasolvent hydrogen transfer reactions (disproportionations) which 1,2-dihydronaphthalene (1,2-DHN) and its dihydrophenanthrene analogues (1,2- and 3,4-DHP) undergo, including:
 - A. Identification of the principal products, and determination of the

identity and extent of formation of side reaction products.

- B. Investigation of the gas and liquid phase kinetics of thermal disproportionation of 1,2-DHN, and the liquid phase kinetics of thermal disproportionation of 1,2- and 3,4-DHP.
 - C. Use of the product identity and kinetic information to infer the most probable mechanism by which the disproportionations occur.
- II. To investigate the conversion of 1,2-DHN into naphthalene (Nap) by model free radical reactions believed to be similar to those that take place during coal hydroliquefaction in a donor solvent, and to conduct analogous investigations with respect to 1,2- and 3,4-DHP.

In these studies, 1,1,2,2-tetraphenyl ethane (TPE) is to be used as the free radical source because it dissociates into diphenylmethyl radicals at temperatures near 300°C where disproportionation is slow.

These studies will include:

- A. Exploratory work to evaluate the feasibility of the study.
- B. Identification of the thermal decomposition products of
 - 1. pure TPE
 - 2. TPE diluted with an inert solvent
 - 3. TPE mixed with Tet
 - 4. TPE mixed with 1,2-DHN
- C. Kinetic studies of the reactions of part B above.
- D. Inference of mechanism through product identity and kinetic information.

R E S U L T S A N D C O N C L U S I O N S

- I. The nature of the intrasolvent hydrogen transfer reactions (disproportionations) which 1,2-DHN and its DHP analogues undergo
 - A. The principal products of the disproportionation of 1,2-DHN (285-

315°C, liquid phase, and 385-410°C, gas phase) are Nap and Tet. Previous work by the author has shown that 1,2-DHN(l), at 165°C in the presence of $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$, gives Nap, Tet, and dimers of 1,2-DHN by a carbonium ion mechanism.¹ Three dimers having the same GC retention times and relative concentrations as the 165°C carbonium ion dimers have been found in the 285-315°C(l) and 385-410°C(g) disproportionation products of pure 1,2-DHN, together with two additional dimers. The formation of dimers from 1,2-DHN in the presence of base², or photolytically³ has been previously reported, but Gill and Hawkins report that the thermal disproportionation of pure 1,2-DHN in the presence of solvents produces Nap and Tet only, in a 1:1 molar ratio.⁴ Our work indicates that thermal disproportionation of 1,2-DHN (307°C) in dodecane solvent gives products consisting of Nap and Tet in a 1:1 ratio, with 17% dimers, and that the disproportionation of pure 1,2-DHN, in the absence of solvents (285-315°C(l), and 385-410°C(g)) produces a Nap:Tet product ratio greater than one, but less than two, together with dimers. The characterization of the dimers is important, since it can be determined from their structures whether they were formed by a carbonium ion or a free radical mechanism. Separation and purification of the dimers has proven to be exceedingly difficult.¹ A further attempt to do this will be made by first separating them with preparative GC, and then purifying them by preparative TLC. (TLC will not separate them, but it is hoped that it will separate the dimers from their decomposition products once the dimers have been separated from each other.)

B. 1. Since the initiation of this grant, previously obtained gas phase kinetic data for the disproportionation of 1,2-DHN ((g), 385-410°C) have been refined as follows:

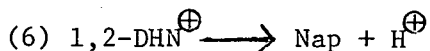
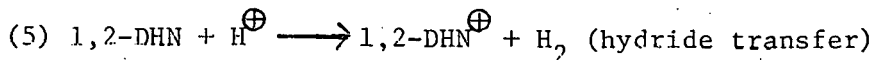
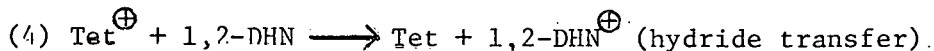
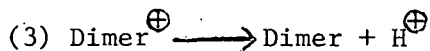
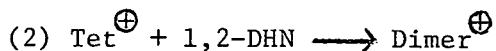
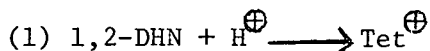
- a) The GC response factors of the reactants and products were reevaluated to confirm that our greater-than-unity Nap:Tet ratios are valid when no solvent is present. The recheck established the response factors to a higher precision than the previous values, and confirmed that the Nap:Tet ratios were indeed correct.
- b) More accurate heat up time corrections have been calculated using the method of Brower.⁵ Heat up time corrections had previously been determined by running tube reactions at various temperatures and concentrations for slightly longer than two minutes (the actual heat up time was approximately two minutes), analyzing the reaction mixtures by GC, and correcting for the reaction that had taken place during heat up. This method is time consuming and tedious. The method of Brower allows one to calculate a t_0 from a time vs temperature heat up curve and an approximate activation energy obtained using a preliminary estimate of t_0 . The calculated t_0 is a time during heat up selected so that the amount of reaction before t_0 is equivalent to the amount of reaction from t_0 until the final temperature is reached, i.e., the uncorrected experimental concentration vs time data are those that would result if the reaction had been started at the calculated t_0 with instantaneous heat up to the final reaction temperature.
- c) New rate constants and activation energies have been calculated.
- B. 2. The rate data indicate that 1,2-DHN disappears by simultaneous first and second order reactions, that Tet and Nap appear by simultaneous first and second order processes with the appearance of Nap having a slightly larger rate constant, and that the dimers appear by

a lower order process than Nap and Tet.

B. 3. Kinetic data for the liquid phase disproportionation of 1,2-DHN (285-315°C) have been collected and are now being analyzed. Preliminary evaluation indicates these data follow relationships similar to those obeyed in the gas phase. Since the analysis is not yet complete, this conclusion is tentative.

B. 4. Small quantities of 1,2- and 3,4-DHP have previously been synthesized (a very long and tedious process). No kinetic studies on these compounds will be initiated until the kinetic work on 1,2-DHN has been finished. This will give a more complete background for the latter investigations, and will hopefully enable the 1,2- and 3,4-DHP to be used most efficiently.

C. The product identification and kinetic data are consistent with a second order disproportionation of 1,2-DHN to give equal quantities of Nap and Tet (this has been proposed to be a concerted, pericyclic reaction^{4,6}) accompanied by a carbonium ion side reaction which has a mechanism similar to that proposed by the author for the 165°C work,¹ i.e.



The source of H^{\oplus} is not known, but could come from traces of water.

The reaction is not surface catalyzed (addition of enough small glass

beads to approximately double the surface area caused no change in rate). It should be noted that the concentration of dimers relative to one another and also as an absolute percentage of the total reaction mixture, and also the greater-than-unity Nap:Tet ratios, which are special features attributed to the carbonium ion mechanism, have shown consistent and reproducible trends throughout the entire history of this research. This has been the case despite the fact that several different batches of reaction tubes and synthesized 1,2-DHN have been used during the course of the work. The source of H^+ , whatever it is, must therefore be consistent and reproducible.

The proposed formation of excess Nap through hydride transfer reaction (5) requires that H_2 be formed in stoichiometric quantities equivalent to the excess Nap. An apparatus to analyze for H_2 is partially assembled, and should be completed soon. Quantitative hydrogen analysis to test the validity of reaction (5) should be underway this summer.

Simultaneous first and second order disappearance of 1,2-DHN with a Nap:Tet product ratio greater than one can also be fit by a multistep, nonchain free radical mechanism. An effort is now being made to arrive at criteria that will allow one mechanism to be selected over the other.

II. The conversion of 1,2-DHN into Nap by free radical reactions believed to model those that take place during coal hydroliquefaction in a donor solvent.

A. Exploratory experiments have been carried out by heating Tet and 1,2-DHN in the presence of TPE (liquid phase, $300^\circ C$). The rate of conversion of 1,2-DHN into Tet and Nap was accelerated relative to blank

runs in the absence of TPE, and the Nap:Tet ratio, relative to the blanks, was also increased. The decomposition of Tet in the presence of TPE was very little different than when no TPE was present. These results indicate that further study is worthwhile, and the experiments listed under II B in the introduction will be initiated. These experiments will likely not get further than the study of the thermal decomposition of pure TPE before the termination of the present grant.

References and Footnotes

1. Wendell H. Wiser and Robert R. Beishline, DOE Contract No. E(49-18)-2006, Final Report, Part D.4.II, Salt Lake City, Utah, in press.

This work has not been published in the open literature because it has been impossible to purify one key dimer. In our hands, the dimers could not be separated by HPLC even though an extensive effort to this end was made. Neither can the dimers be separated by TLC. They are separated by GC, but the high temperatures and relatively long retention times necessary for elution on a preparative scale cause partial decomposition. One of the dimers crystallizes out of the impure elution mixture, and has been well characterized. The other key dimer has been sufficiently purified to get a good NMR and thereby infer its structure, but it has not been purified sufficiently for elemental analysis. (A third dimer is present in smaller amounts. No effort has been made to characterize it except to determine its molecular weight by mass spec.)

A final attempt will be made to purify the dimer in question by the procedure outlined in the last part of RESULTS, I.A. of this report. The work will then be submitted for publication whether or not that attempt is successful.

2. Lawson G. Wideman, J. Org. Chem., 35, 1698 (1970).
3. Johannes Dekker and Theodor G. Dekker, J. So. African Chem. Inst., 26, 25 (1973).
4. G. Byron Gill and Stephen Hawkins, J.C.S. Chem. Comm., 1974, 742.
5. K. R. Brower, J. Org. Chem., 45, 1004 (1980).
6. Preetinder S. Virk, Fuel, 58, 149 (1979).

Seminar Presentations

A seminar consisting essentially of the contents of this report will be presented at Battelle Pacific Northwest Laboratories on August 4, 1980.

Publications

None

Manuscripts in Preparation for Publication

The Zinc Chloride Catalyzed Decomposition of 1,2-Dihydronaphthalene at 165°C. A Coal-related Model Compound Study.

Robert R. Beishline*, Brian Gould, Edward B. Walker, Douglas K. Stuart, Joanna Schultzski, John Shigley, Don K. Dalling and Larry L. Anerson

This manuscript (copy enclosed) has not been submitted for publication because it has not been possible to obtain one key dimer (a new compound) in sufficient purity for elemental analysis. A proposed method to purify the compound is noted in this report (see RESULTS AND CONCLUSIONS, section I.A.). Using this method, a final attempt will be made to purify the compound. The work will then be submitted for publication whether or not that attempt is successful.