

## AN INVESTIGATION INTO THE REACTIVITY OF ISOTETRALIN

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### ABSTRACT

Molecular orbital calculations were used to explore proposed reaction mechanisms of isotetralin (ISO) and tetralin (TET). Heats of formation and electronic data were determined for ground states and intermediate species. Since the reaction mechanisms was not known a priori, calculations were performed for anionic, cation and free radical dehydrogenation mechanisms. The electron density in the frontier molecular orbitals was used to assess the relative reactivity of sites within ground state and radical species. Model reactivity studies examining the thermal and catalytic reactivity of ISO and TET were performed. ISO was much more reactive than its isomeric analogue TET. Possible reaction pathways are proposed based upon the product slate obtained in the model compound reactivity experiments that were performed at 225, 380 and 425°C with ISO, TET, 1,4-dihydronaphthalene and 1,2-dihydronaphthalene. The results from the experimental study were evaluated in light of the results obtained from the molecular orbital calculations.

### INTRODUCTION

The cyclic olefin, isotetralin, (1,4,5,8-tetrahydronaphthalene) is a highly effective donor for coal conversion at liquefaction temperatures. In previous experimental work, isotetralin converted more coal to THF solubles under thermal liquefaction conditions in both nitrogen and hydrogen than did tetralin (1,2). The results of experimentally evaluated reactivities and reaction pathways under a variety of conditions have recently been reported by Bedell and Curtis (2). The observed high reactivity and hydrogen donability of isotetralin warrants further investigation to understand its mechanism of hydrogen donation and a subsequent investigation of how that information can be applied to processing.

The focus of this report is to examine the dehydrogenation mechanism of ISO and TET using molecular orbital calculations and to compare the calculated results with those obtained experimentally. To achieve this goal, calculations were performed using a semi-empirical method of modified neglect of diatomic overlap (MNDO), developed by Dewar and Thiel (3). The second part of the investigation determined the most likely site for hydrogen donation from each donor molecule, by using frontier molecular orbital electron densities (4).

### EXPERIMENTAL RESULTS

**Isotetralin Reactivity.** Isotetralin (ISO) showed much greater reactivity than did tetralin when reacted at temperatures of 225 and 380°C under both nitrogen and hydrogen atmospheres in stainless steel tubing bomb reactors at different reaction times. ISO converted rapidly and formed the reaction products of 1,2-dihydronaphthalene (1,2-DHN), 1,4-dihydronaphthalene (1,4-DHN), tetralin (TET) and naphthalene (NAP). The same products were formed regardless of the atmosphere, but different amounts were present as shown in Table 1. After two minutes of reaction at 380°C in either nitrogen or hydrogen, nearly 50% of the ISO converted producing 1,4-DHN as

the primary product. Longer reaction times in either nitrogen or hydrogen resulted in all of the ISO being converted. Conversely, TET showed little reactivity at 380 or 425°C. Even after 30 minutes of reaction in either atmosphere at 380°C, less than 5% conversion of TET was obtained. Reactions of TET for 15 minutes at 425°C resulted in 20% conversion in nitrogen and ~ 12% in hydrogen. The products formed in each case were 1,2-DHN, 1,4-DHN and NAP.

**Reaction Pathway for Isotetralin.** A proposed thermal dehydrogenation reaction pathway based on the products obtained from reactions performed with ISO at 225 and 380°C in nitrogen and hydrogen atmospheres is presented in Figure 1. In addition, reactions were performed using reaction products from ISO as the reactants to further elucidate the reaction pathway. The product distributions from reactions involving 1,2-DHN and 1,4-DHN are presented in Table 2. Short time (2 minute) reactions of 1,4-DHN in either nitrogen or hydrogen at 225 or 380°C resulted in ~ 25% or less of the 1,4-DHN being converted to the products, NAP and 1,2-DHN. No TET was formed. The reaction products observed from a 30 minute reaction of 1,4-DHN at 380°C were TET, 1,2-DHN, and NAP in hydrogen and NAP and TET in nitrogen; 1,4-DHN readily isomerized to 1,2-DHN. More NAP was produced in nitrogen than in hydrogen and substantially more TET was produced from 1,4-DHN in hydrogen after 30 minutes of reaction than in nitrogen.

The reaction of 1,2-DHN was also examined under a variety of conditions as presented in Table 2. Thermal reactions were performed at 425°C for 15 minutes while catalytic reactions using two different hydrogenation catalysts were performed at 225 and 380°C for short 2-minute reactions. Under catalytic conditions in hydrogen, 1,2-DHN preferentially produced TET as a product while under thermal conditions NAP was the preferred product. Some isomerization of 1,2-DHN to 1,4-DHN did occur indicating that the isomerization pathway to TET may also be available.

The thermal reactions of TET shown in Table 1 are inconclusive of a preferential pathway for TET reaction to 1,2-DHN. This pathway is obscured because of the observed isomerization of 1,2-DHN to 1,4-DHN. However, the reaction of 1,2-DHN particularly under catalytic conditions indicated that TET was the preferred product. On the basis of microscopic reversibility, it would be appropriate to suggest that TET may preferentially form 1,2-DHN in the dehydrogenation reaction.

The thermal dehydrogenation pathway of ISO proposed then is (1) the isomerization of ISO to form TET as indicated by the formation of TET in the 380°C reactions in both nitrogen and hydrogen and in (2) the dehydrogenation of ISO to form 1,2-DHN or 1,4-DHN as indicated by both the short time and longer reaction products in both atmospheres. 1,4-DHN appeared to be the favored product except at 60 minute reaction time in hydrogen. The isomerization step from ISO to TET in the pathway resulted in further dehydrogenation of TET to 1,2-DHN or 1,4-DHN. The DHN's then dehydrogenated to form NAP as indicated by the dehydrogenation of 1,4-DHN to NAP at all reaction conditions.

## MOLECULAR ORBITAL CALCULATIONS

It has been reported in the literature on polyaromatic hydrocarbons that the electron density in the frontier molecular orbitals of the carbon or heteroatoms can be used, with some degree of success as an indicator of reactivity (4, 6-8). Sato et al. (6) found good agreement between the experimentally determined reactivity ranking of 1-methylnaphthalene, tetralin, decalin, and 9,10-dihydroanthracene, with that predicted by the electron density in the frontier molecular orbitals. Obara et al. (7) experimentally found that for a series of compounds, the ease of hydrogenation was acenaphthylene > anthracene > phenanthrene, and reported that "this order is in good agreement

with that in the terms of frontier electron density at a given position of the compounds" (7). Sukano et al. (8) found that the conversion of the donor increased with increasing electron density of the carbon and oxygen atoms of the carbonyl groups in the hydrogen acceptors.

Molecular orbital (MO) calculations were performed to elucidate the reasons for the greater reactivity observed for ISO in comparison to TET and to more fully investigate the dehydrogenation pathway proposed from experimental results. These MO calculations were performed using SYBYL (licensed from Tripos Associates, Inc.), which is an integrated molecular modeling package with graphics and interfaces to various computational methods. The desired structures were input using the graphics capabilities of SYBYL, with standard bond lengths and angles. These structures were next optimized using the Tripos 5.2 force-field (5) and conjugate gradient minimization. The resulting optimized structures were used as input to AMPAC (QCPE 506) using the MNDO Hamiltonian, with complete geometry optimization. MO calculations were performed on a VAX 5320 computer, while the force-field calculations were done on a MicroVaxII and Sparcstation 1+ workstation.

Since the actual dehydrogenation mechanism was not known a priori, three separate routes were investigated; they were cationic, anionic, and two proposed free radical pathways. MNDO calculations were performed on the ground state reactants (ISO or TET), the single radical or charged intermediate, the bi-radical or dual charge species, and finally the ground state product. The molecular orbital procedures used are capable of determining energetic, electronic and structural data. For the current investigation, the thermodynamic stability of each step was assessed through heats of formation.

Calculations on the open shell species (free radicals) were performed using the half electron approximation, in which the unpaired electron is represented by two "half electrons" with opposite spin. The repulsive energy introduced by this convention is subtracted from the final energy value. The energies calculated in this way can be directly compared to those for closed shell species.

Frontier orbital density was determined as the electron density in the highest occupied molecular orbital (HOMO) for closed shell species, and the singly occupied molecular orbital (SOMO) for radicals. These values are determined as the sum of squares of the atomic orbital coefficients for a given atom. These values are multiplied by one and two for open and closed shell structures, respectively.

#### DEHYDROGENATION MECHANISM

Based on the experimental results that have been previously discussed and presented in Figure 1, MNDO calculations were performed for the transitions between reactants and products from ISO to 1,4-DHN and TET to 1,4-DHN, and the other dehydrogenation paths illustrated. Initial work focused on the former pathways, since they appear to be preferred to the 1,2-DHN pathway. As indicated, cationic, anionic, and radical routes were examined. The calculated heats of formation for the proposed compounds in each step are shown in Figures 2 and 3.

**Frontier Orbital Electron Density Calculations.** Based on these results, the distribution of electron densities was examined for each step in the free radical pathway. As indicated in the cited literature, it has been proposed that the higher the frontier electron density  $Fr(R)$ , the more reactive the site; i.e., the hydrogen most likely to be removed will have the highest electron density. The results of these frontier orbital electron density calculations for ISO and TET are presented in Figures 4 a-d and 5 a-e, respectively.

Figure 4-a shows the frontier electron density for the donable hydrogen in ground state ISO. As can be seen, the hydrogen on carbons 1,4,5, and 8 are approximately equivalent, and the loss of a hydrogen is not expected to be preferential to any one of the four positions. For illustrative purposes, if the hydrogen is lost from carbon 8, the radical species shown in Figure 4-b will be formed. Evaluating the resulting electron densities, the second hydrogen will be lost from carbon 5, which has the highest electron density. The resulting bi-radical species formed is shown in Figure 4-c. Once this species is formed, the double bond will isomerize to either the 7-8 or 5-6 positions, both of which are equivalent. The new bi-radical species formed is shown in Figure 4-d, and once the radicals are on adjacent carbon centers, a double bond will form to produce 1,4-DHN (Figure 4-e). These frontier molecular orbital electron density calculations predict that ISO will dehydrogenate preferentially to 1,4-DHN which is in good agreement with the experimental results.

Figure 5-a shows Fr(R) for the donable hydrogen in ground state TET. The electron densities for the hydrogen atoms at carbons 1 and 4, using the IUPAC numbering system for naphthalene parent compound are greater than those of the hydrogen atoms on carbons 2 and 3. Assuming that the loss of hydrogen occurs at the position with the highest electron density indicates that dehydrogenation occurs at carbon 4. Removal of the hydrogen at carbon 4 level forms the single radical species shown in Figure 5-b. It is predicted that the second hydrogen will be removed from carbon 3, the position with the highest electron density in the single radical species, to form the bi-radical shown in Figure 5-c. Once the bi-radical species is formed, the free electrons will combine to form a double bond, producing 1,2-DHN (Figure 5-d). The frontier orbital electron density calculations predict that TET will preferentially be dehydrogenated to 1,2-DHN, which appears to be what the experimental results previously described suggest. From the calculations for the frontier orbital electron density of ISO and TET, and the comparison with experimental results, Fr(R) appears to be a useful predictive and explanatory tool in the investigation of the dehydrogenation of cyclic olefins and hydroaromatic compounds.

#### SUMMARY OF THEORETICAL STUDY

The MNDO calculations, coupled with the frontier molecular orbital electron density calculation, are in good agreement with the experimentally determined results in the following points: 1) ISO is readily converted to 1,4-DHN and TET, and only to a small extent to 1,2-DHN. 2) TET is preferentially converted to 1,2-DHN. 3) ISO is more reactive than TET because of its lower energy barrier for 1,4-DHN formation, more possible reaction pathways, and its larger Fr(R) value on the greater number of donable hydrogen. These results illustrate the potential of molecular orbital calculations to be a useful tool in the understanding of fundamental dehydrogenation chemistry of model hydrogen donor compounds.

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Table 1. Reactivity of Isocetralin and Tetralin

Donor	Temperature (°C)	Atmosphere	Time (min)	NMP	1,2-DH	1,4-DH	TEF	ISO
ISO	225	H <sub>2</sub>	2	0.0	0.0	2.8(0.3)	0.0	97.2(0.3)
	380	H <sub>2</sub>	2	2.0(0.1)	0.0	48.4(0.3)	1.6(0.1)	46.4(0.3)
	380	H <sub>2</sub>	30	55.1(1.5)	4.0(0.5)	36.7(1.0)	3.6(0.4)	0.0
ISO	225	H <sub>2</sub>	2	0.0	0.0	1.7(0.3)	0.0	98.3(0.3)
	380	H <sub>2</sub>	2	2.2(0.2)	3.1(0.7)	39.1(1.8)	3.3(1.5)	52.3(2.9)
	380	H <sub>2</sub>	15	30.5(0.5)	23.8(4.6)	27.9(12.3)	17.8(6.0)	0.0
	380	H <sub>2</sub>	30	52.8(2.3)	10.0(2.6)	26.8(3.7)	10.6(1.2)	0.0
	380	H <sub>2</sub>	60	61.1(2.1)	11.5(1.7)	1.1(0.3)	26.3(3.5)	0.0
TEF	380	H <sub>2</sub>	30	0.8(0.2)	0.0	0.0	99.2(3.8)	0.0
	425	H <sub>2</sub>	15	1.2(0.02)	12.5(0.6)	6.3(0.6)	80.0(1.2)	0.0
TEF	380	H <sub>2</sub>	30	0.7(0.1)	1.0(0.1)	2.1(0.3)	96.2(2.3)	0.0
	425	H <sub>2</sub>	15	0.0	3.5(0.2)	8.6(0.1)	87.5(0.3)	0.0

Table 2. Reactivity of 1,4-Dihydronaphthalene and 1,2-Dihydronaphthalene

Donor	Temperature (°C)	Atmosphere	Time (min)	Catalyst	NMP	1,2-DH	1,4-DH	TEF	ISO
1,4-DH	225	H <sub>2</sub>	2	none	10.7(1.7)	10.9(0.3)	78.4(1.5)	0.0	0.0
	380	H <sub>2</sub>	2	none	13.1(0.2)	11.3(0.2)	75.4(0.2)	0.0	0.0
	380	H <sub>2</sub>	30	none	60.2(11.7)	0.0	28.5(11.6)	11.3(0.8)	0.0
1,2-DH	225	H <sub>2</sub>	2	none	9.2(0.3)	11.0(0.2)	79.8(0.3)	0.0	0.0
	380	H <sub>2</sub>	2	none	13.0(0.2)	12.8(0.9)	74.2(1.1)	0.0	0.0
	380	H <sub>2</sub>	30	none	44.9(0.3)	11.5(0.3)	1.7(0.5)	41.9(0.6)	0.0
1,2-DH	425	H <sub>2</sub>	15	none	43.6(0.04)	42.4(0.3)	9.1(0.3)	4.7(0.1)	0.0
	425	H <sub>2</sub>	15	none	40.2(0.6)	46.1(0.8)	8.2(0.3)	4.8(0.1)	0.0
1,2-DH	225	H <sub>2</sub>	2	MoAl <sub>2</sub> O <sub>3</sub>	trace	44.7(0.4)	trace	55.3(0.4)	0.0
	380	H <sub>2</sub>	2	MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.0	17.3(8.5)	3.1(0.5)	79.6(8.0)	0.0
	380	H <sub>2</sub>	2	MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	99.9(4.7)	0.0
1,2-DH	380	H <sub>2</sub>	2	MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	9.1(4.7)	0.0	0.0	90.9(4.7)	0.0

Reaction Conditions: 425 cps, 1250 psig H<sub>2</sub> or H<sub>2</sub> charge at ambient temperature, 2.0 g charge of 0.5 weight percent double hydrogen in hexadecane.

Abbreviations:

NMP = naphthalene; 1,2-DH = 1,2-dihydronaphthalene; 1,4-DH = 1,4-dihydronaphthalene; TEF = tetralin; ISO = Isocetralin.

Figure 1. REACTION PATHWAY FOR ISOTETRALIN.

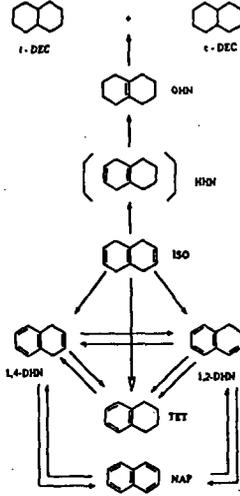


Figure 2. HEAT OF FORMATION DATA FOR THE TRANSITION OF ISO TO 1,4-DHN: THREE MECHANISMS.

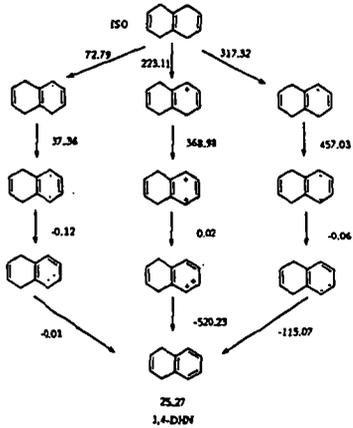


Figure 3. HEAT OF FORMATION DATA FOR THE TRANSITION OF TET TO 1,4-DHN: THREE MECHANISMS.

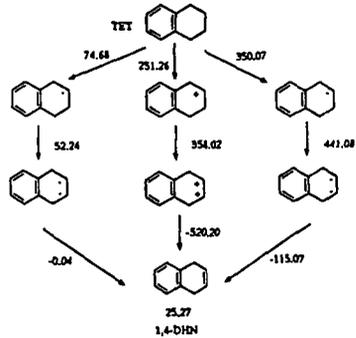


Figure 4. ELECTRON DENSITIES IN THE TRANSITION OF ISO TO 1,4-DHN .

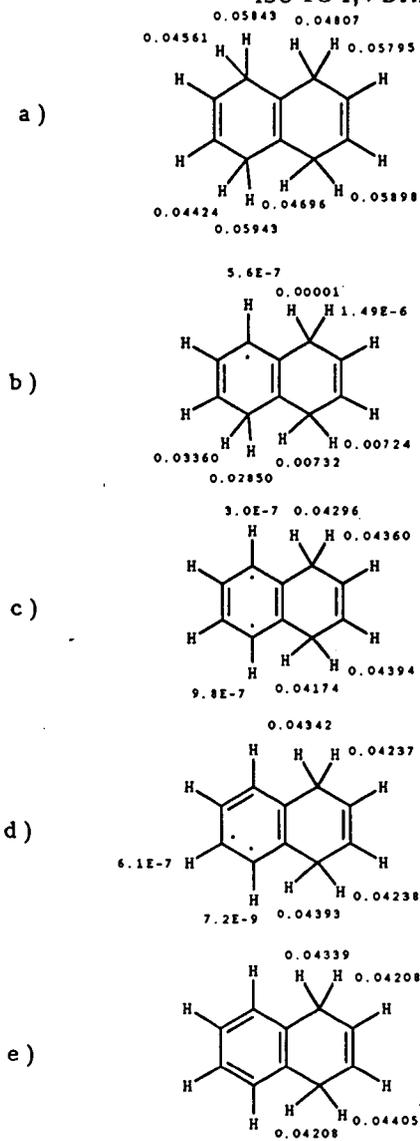


Figure 5. ELECTRON DENSITIES IN THE TRANSITION OF TET TO 1,2-DHN.

