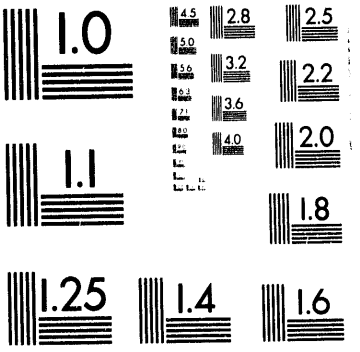
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COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

Quarterly Report
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Task I. Elucidation of Hydrogen Transfer Reactions in Coprocessing

The objective of this task was to attain a fundamental understanding of the hydrogen transfer reactions that occur during coprocessing and to elucidate their role and importance in achieving upgraded products.

Subtask I.A. Hydrogen Transfer from Cycloalkanes

Introduction

The research conducted during this quarter evaluated hydrogen transfer from hydroaromatics and cyclic olefins to aromatics under thermal and catalytic conditions. The reactions under study involved thermal reactions of a cyclic olefin, isotetralin (ISO), with aromatics, anthracene (ANT) and pyrene (PYR). These reactions completed a set of experiments with hydrogen-rich species and aromatics previously reported that included cycloalkanes of perhydropyrene (PHP) and perhydroanthracene (PHA), hydroaromatic donors, tetralin (TET) and dihydroanthracene (DHA), cyclic olefins, hexahydroanthracene (HHA) and ISO, and aromatics, PYR and ANT.

Catalytic reactions performed this quarter used a sulfur catalyst that had been shown by Rudnick to affect the hydrogen transfer from cycloalkanes to aromatics and/or coal. Rudnick[1,2] investigated the dehydrogenation of alicyclic compounds converting them to the corresponding aromatic compounds in a process in which the alicyclic compounds served as hydrogen donors. Thiophenol and thiol were effective catalysts and helped promote the conversion of alicyclic compounds to aromatic compounds. For example, decahydropyrene was converted to pyrene, 4,5-dihydropyrene or 4,5,9,10-tetrahydropyrene. The reactions were performed at elevated

temperatures (440°C) and in the liquid phase; when necessary superatmospheric pressure of an unspecified gas was used to maintain the reactants in the liquid phase.

This invention was illustrated by the following example. Perhydropyrene (PHP) was reacted with benzophenone as a model hydrogen acceptor. The reaction conditions were temperature of 440°C and residence time of 60 minutes. No pyrene was formed from PHP under these conditions. The same reaction was performed in the presence of thiophenol at 0.51 weight percent. The result showed that the products contained 94.7% diphenylmethane, the hydrogenated product of benzophenone, and some pyrene present. This work was repeated in our laboratory during this quarter.

The research performed in our laboratory focused on evaluating the effect of a sulfur catalyst on the transfer of hydrogen from cycloalkanes like perhydropyrene (PHP) to aromatics like anthracene under catalytic conditions. The catalyst used in this study was sulfur generated from thiophenol present at a concentration level of 2000 ppm of sulfur. The reactions were performed under two temperature conditions, 380 and 440°C; both thermal and catalytic reactions were performed for comparison. In addition, the individual cycloalkane and aromatic compounds were reacted under these conditions so that a direct comparison of the effect of temperature and of catalyst on the reaction products formed could be made.

Hydrogen Transfer from Cyclic Olefins

The research performed during this quarter focused on examining reactions of ISO with ANT and PYR which were performed in both nitrogen and hydrogen atmospheres. The cyclic olefin and aromatic were introduced at ratios of 1 to 1 and 5 to 1 weight ratio of ISO to ANT and of ISO to PYR. The reactions were conducted in small tubular microreactors made of 316

stainless steel and equipped with a metering valve for introducing either hydrogen or nitrogen into the system. The reaction conditions were a reaction temperature of 380°C, reaction time of 30 or 90 minutes, agitation at 435 cpm and 400 psig H_2 or N_2 charged at ambient conditions. All reactions were duplicated and some were replicated more times. The reaction products were analyzed by gas chromatography using the internal standard method for quantitation. Qualitative analysis was performed by comparing retention times with authentic compounds or by GC mass spectrometry analysis.

ISO was reacted individually and combinatorially with ANT and PYR. ISO was reacted individually first under these reaction conditions and completely converted forming the reaction products of naphthalene (NAP), 1,2-dihydronaphthalene (1,2-DHN), 1,4-dihydronaphthalene (1,4-DHN) and tetralin (TET) as shown in Table 1. The primary product was NAP, with more NAP being formed under nitrogen than under hydrogen. The secondary product was dihydronaphthalene with the 1,4-DHN being the predominant isomer.

Total conversion of ISO was also achieved when ISO was reacted with ANT at both 1 to 1 and 5 to 1 weight ratios of ISO to ANT in both hydrogen and nitrogen atmospheres (Table 1). NAP was the primary product at both ratios but more NAP was produced at the 1 to 1 ratio than at the 5 to 1 ratio. In the 5 to 1 ratio reaction, ~ 20 mole % TET was formed which was double that formed in the reaction with the 1 to 1 ratio. At both ratios, a small amount of decalin (DEC) was formed. Hence, at the higher ratio less dehydrogenation of ISO occurred.

ANT underwent some hydrogenation in a hydrogen atmosphere as shown in Table 2. The primary product was dihydroanthracene (DHA). However, considerably more hydrogenation of ANT occurred in the presence of ISO in both atmospheres. In the reactions

with a 1 to 1 ratio, more than 70% of the ANT converted to DHA and tetrahydroanthracene (THA) with the predominant product being DHA. More than 90% conversion occurred in the 5 to 1 ratio, with more conversion occurring in hydrogen than in nitrogen. DHA was the predominant product in the 5 to 1 ratio, although five times more THA was formed in nitrogen than in hydrogen.

The reaction of ISO with PYR yielded a product distribution from ISO that contained the same molecular species as the ISO reactions with ANT as also shown in Table 2. However, the product distribution was more variable in the two different atmosphere with PYR present than with ANT present. With the 1 to 1 ratio of ISO to PYR, 66% NAP was formed in nitrogen while only 57% was formed in hydrogen. 1,4-DHN was the predominant product from ISO in both atmospheres but more was produced in hydrogen than in nitrogen. With the 5 to 1 ratio of ISO to PYR, less NAP (48%) was formed in nitrogen than in hydrogen where 58% was formed. 1,4-DHN was the secondary product in nitrogen while TET was the secondary product in hydrogen.

When reacted by itself, PYR showed no reaction in either nitrogen or hydrogen (Table 3). By contrast, in the presence of ISO, substantial reactivity of PYR was observed. More than 12% conversion of PYR to dihydropyrene (DHP) and tetrahydropyrene (THP) was obtained with a 1 to 1 ISO to PYR ratio. More conversion occurred in hydrogen than in nitrogen, but DHP was the primary product in each atmosphere. Reaction of PYR with ISO at a 5 to 1 ISO to PYR ratio yielded more than 40% conversion in hydrogen and more than 30% conversion in nitrogen. DHP was the primary product in both atmospheres but THP and hexahydropyrene (HHP) were also formed.

One last set of reactions were performed in which the reaction time for the reaction of ISO with ANT and ISO with PYR was increased from 30 to 90 minutes. The products achieved were the same as the shorter reaction of 30 minutes but more reaction occurred after 90 minutes as shown in Tables 4 and 5.

A comparison of the percent hydrogenation of the aromatics in the different reaction systems is given in Table 6. The percent hydrogenation is defined as the number of mole of hydrogen required to achieve the liquid products as a percentage of the moles of hydrogen needed to produce the most hydrogenated product. More hydrogenation was observed in the hydrogen atmosphere than in the nitrogen atmosphere and more at 90 minutes than at 30 minutes.

Reaction of Perhydropyrene with Benzophenone

The reactions of perhydropyrene (PHP) with benzophenone (BEN) used in the European patents by Rudnick[1,2] were replicated in our laboratory. The reaction conditions given in the patent were followed as closely as possible. The conditions were a reaction temperature of 440°C, reaction time of 60 minutes, and a catalyst of thiophenol being present at 0.51 wt%. The PHP and BEN were introduced in 0.42 mole ratio of BEN to PHP. The reactions were performed under nitrogen at 400 and 1250 psi charged at ambient temperature and under hydrogen at 400 and 1250 psi charged at ambient temperature.

The reactions under nitrogen allowed for evaluating the hydrogen transfer directly from the cycloalkane, PHP, to the acceptor, BEN. The reactions were performed thermally and catalytically as presented in Table 8. At both pressures more reaction of the BEN was observed

in the catalytic reaction than in the thermal reaction. The reaction product was diphenylmethane (DPM). In the most reactive case, only slightly more than 5% DPM was produced.

Under the hydrogen, more conversion of BEN to DPM occurred than the nitrogen atmosphere. As with the reactions in nitrogen, the catalytic reactions with hydrogen showed more conversion of BEN than did the thermal reactions. The higher pressure of hydrogen also resulted in more reaction of BEN than did the reactions at lower hydrogen pressure. The most reaction was observed in the catalytic reaction with hydrogen charged at 1250 psi at ambient temperature where more than 30% of the BEN was converted to DPM. This reactivity is demonstrated in Figure 1 where the mole percent of DPM produced from the reactions of PHP and BEN is presented at the different reaction conditions.

Regardless of the amount of BEN reacted, the amount of PHP reacted was never any more than 1.5% of the PHP charged. The reaction products were hexahydropyrene (HHP) and pyrene (PYR). The PYR was only observed in the reactions with a nitrogen atmosphere. The reaction conditions of these experiments did not replicate the conditions of the patent exactly since the conditions were not explicitly stated in the patent. Of the eight reaction conditions tested, none of the reactions came close to achieving the 94% DPM production described in the patent.

Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 380°C

Thermal and catalytic reactions of perhydropyrene (PHP) and anthracene (ANT) were performed individually and combinatorially at 380°C. The catalytic reactions were performed with 2000 ppm sulfur introduced as thiophenol. The reactions were performed under both

hydrogen and nitrogen atmospheres. The product distributions obtained under these various reaction conditions at 380°C are given in Table 9.

The thermal and catalytic reactions of PHP yielded no products under either atmosphere. By contrast, ANT produced more than 11% DHA in a thermal reaction with hydrogen and less than 0.5% DHA with nitrogen. The presence of sulfur in the reaction increased the amount of DHA in both atmospheres to 16.7% for hydrogen and 1.9% for nitrogen.

The combined reaction of PHP with ANT in a 1 to 1 ratio yielded some products in the thermal and more in the catalytic reaction. As in the individual reactions, the hydrogen atmosphere had a substantial effect on the reactivity of ANT but had little effect on PHP. The addition of 2000 ppm sulfur catalyst increased the amount of hydrogenation of ANT to DHA under both atmospheres. The catalyst also increased the amount of dehydrogenation of PHP. Under the thermal conditions, PHP only produced pyrene (PYR) as a product, while under catalytic conditions, hexahydropyrene (HHP) was formed in larger amounts than PYR.

The reaction of PHP with ANT in hydrogen at a 5 to 1 PHP to ANT ratio showed a substantial effect with the catalyst. ANT yielded 16% DHA under thermal hydrogen conditions but nearly 44.5% DHA under catalytic conditions. A large increase was also observed in nitrogen where only 2.5% DHA was formed thermally but more than 17.6% was formed catalytically. For PHP, HHP was produced in the catalytic reaction while only PYR was formed thermally. Hence, substantial amounts of hydrogen were transferred from PHP to ANT under catalytic reaction conditions.

Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 440°C

The higher reaction temperature resulted in more reaction products from ANT as shown in Table 10. Under a hydrogen atmosphere and reacted both thermally and catalytically, ANT hydrogenated to DHA, THA and OHA while under nitrogen only DHA was formed. The effect of the sulfur catalyst at 440°C was not as pronounced at it was at 380°C. A small increase in the amount of hydrogenation occurred for ANT. No effect of the catalyst or increased reaction temperature was observed on PHP in the individual reactions.

In the thermal and catalytic reactions with 1 to 1 PHP to ANT ratio, ANT hydrogenated to DHA under hydrogen and nitrogen. In both the thermal and catalytic reactions, the amount of DHA formed was larger than in individual reaction of ANT; this increase was particularly apparent in the nitrogen atmosphere. Hence, some hydrogen transfer was occurring from PHP to ANT. The effect of the catalyst was minimal at 440°C in the reaction with hydrogen, but the catalyst promoted an increase in DHA in the catalytic nitrogen reaction forming 5.9% DHA compared to 1.2% in the thermal nitrogen reaction. PHP yielded HHP in both the thermal and catalytic reactions at 440°C. Increased conversion of PHP and increased amounts of HHP were formed in the catalytic reactions for both the nitrogen and hydrogen atmospheres.

In the combined PHP to ANT reactions at a 5 to 1 ratio of PHP to ANT, no effect of the catalyst was observed in the reactions using a hydrogen atmosphere; however, the catalyst did promote hydrogenation of ANT to DHA and small amount of increased reactivity of PHP in the nitrogen atmosphere.

hydrogen acceptor. The values from this calculation are given in the column designated as Definition 1 in Table 16. The results from definition one are shown in Figure 5. The higher temperature reactions showed higher amounts of gaseous hydrogen incorporated into the ANT reaction products than did the lower temperature reactions. The second definition used subtracted the moles of hydrogen accepted by the hydrogen acceptor in nitrogen from the moles of hydrogen accepted by the acceptor in hydrogen. The results from definition 2 are shown in Figure 6. This definition also showed that the acceptor ANT in the higher temperature reaction accepted more gaseous hydrogen than did the ANT in the lower temperature reactions.

Summary

ISO, a cyclic olefin, was an effective hydrogen for aromatic species at 380°C. ANT, a readily hydrogenated aromatic under these reaction conditions, showed substantial reactivity in the presence of ISO both in hydrogen and nitrogen atmosphere. PYR, a more difficult to hydrogenate aromatic species, did accept hydrogen from ISO. PYR showed 6.02 and 17.3% hydrogenation in hydrogen and 4.11 and 13.2% hydrogenation in nitrogen when ISO was present in 1 to 1 and 5 to 1 weight ratios, respectively. These results are in contrast with those obtained from PYR in the presence of TET where essentially no hydrogenation of PYR occurred. Likewise, ISO had a substantial effect on the hydrogenation of ANT yielding 18 to 19% hydrogenation at the 1 to 1 ratio in both hydrogen and nitrogen and ~ 24% hydrogenation at the 5 to 1 ratio in both hydrogen and nitrogen. By contrast, less than 5% hydrogenation of ANT was the highest hydrogenation observed in the reactions with TET and ANT. The percent hydrogenation of the aromatics, PYR and ANT, increased with time in the presence of ISO in both hydrogen and nitrogen atmospheres. Similar results were obtained with the cyclic olefin,

HHA, that were reported previously. HHA yielded substantially more hydrogenation of PYR in a hydrogen atmosphere than did DHA.

The effect of the sulfur catalyst on promoting hydrogen transfer from the cycloalkane perhydropyrene to the aromatic anthracene was greater at 380°C than at 440°C. The impact of the sulfur catalyst was more obvious in a nitrogen than in the hydrogen atmosphere. The same statement is true also for the reactions with a 1 to 1 of PHP to ANT than with the 5 to 1 ratio. However, promotion of hydrogen transfer from PHP to BEN by thiophenol was only partially successful when compared to the results obtained by Rudnick.

References

1. Rudnick, L. R.; Mobil Oil Corp., USA, "Hydrogenation," Eur. Pat. Appl. EP195539 A2 24 Sep 1986a.

2. Rudnick, L. R.; Mobil Oil Corp., USA, "Conversion of Alicyclic Compounds into Aromatic Compounds," Eur. Pat. Appl. EP195541 A1, 24 Sep 1986.

Table 1. Product Distributions for Reactions of Isotetralin and Isotetralin with Anthracene for 30 Minute Reactions

Compound/ Conditions	Product Distributions, mole %					
	NAP	1,2-DHN	1,4-DHN	TET	ISO	DEC
ISO						
H_2	51.91(1.33)	4.05(0.35)	34.13(0.89)	9.91(1.10)	0.00(0.0)	0.00(0.00)
N_2	57.47(0.18)	3.38(0.52)	32.33(0.27)	6.79(0.80)	0.00(0.0)	0.00(0.00)
ISO/ANT (1:1)						
H_2	63.52(0.11)	8.47(0.22)	16.11(0.13)	10.28(0.10)	0.00(0.0)	1.58(0.08)
N_2	63.02(0.63)	8.74(0.15)	15.93(0.43)	10.76(0.14)	0.00(0.0)	1.51(0.01)
ISO/ANT (5:1)						
H_2	51.48(0.68)	12.13(0.29)	11.09(0.30)	22.30(0.58)	0.27(0.03)	2.69(0.12)
N_2	51.37(0.35)	12.73(0.07)	12.67(0.71)	20.31(0.25)	0.19(0.07)	2.68(0.04)
ISO/PYR (1:1)						
H_2	56.91(0.66)	4.27(0.05)	30.00(0.43)	7.90(0.98)	0.00(0.0)	0.89(0.06)
N_2	66.17(1.86)	3.69(0.10)	22.83(1.22)	6.37(0.58)	0.00(0.0)	0.92(0.05)
ISO/PYR (5:1)						
H_2	57.54(1.52)	9.37(0.21)	12.41(2.45)	18.60(1.27)	0.00(0.0)	2.04(0.18)
N_2	48.13(0.30)	9.39(0.16)	25.75(0.44)	14.87(0.27)	0.00(0.0)	1.81(0.09)

Reaction conditions: 380°C, 435 cpm, 30 minutes, 400 psig H_2 or N_2 charged at ambient conditions.

ANT = anthracene, ISO - isotetralin, NAP = naphthalene, 1,2-DHN = 1,2-dihydronaphthalene, 1,4-DHN = 1,4-dihydronaphthalene
TET = tetralin, DEC = decalin.

Numbers in parentheses indicate standard deviations.

Table 2. Product Distributions for Reactions of Anthracene and Anthracene with Isotetralin for 30 Minute Reactions

Product Distributions, mole %			
Compound/ Conditions	ANT	DHA	THA
ANT			
H_2	88.31(1.07)	11.68(1.06)	0.00(0.00)
N_2	99.53(0.76)	0.47(0.16)	0.00(0.00)
ISO/ANT (1:1)			
H_2	25.84(1.07)	71.31(1.06)	2.83(0.10)
N_2	29.51(0.49)	67.69(0.39)	2.79(0.12)
ISO/ANT (5:1)			
H_2	1.18(0.28)	98.08(0.30)	0.72(0.05)
N_2	7.90(0.71)	86.60(0.70)	5.48(0.08)

Reaction conditions: 380°C, 435 cpm, 30 minutes, 400 psig H_2 or N_2 charged at ambient conditions.

ANT = anthracene, DHA = dihydroanthracene, THA = tetrahydroanthracene, ISO = isotetralin.

Numbers in parentheses standard deviations.

Table 3. Product Distributions for Reactions of Pyrene and Pyrene with Isotetralin for 30 Minute Reactions

Compound/ Conditions	Product Distributions, mole %			
	HHP	THP	DHP	PYR
PYR				
H_2	0.00(0.00)	0.00(0.00)	0.00(0.00)	100.00(0.00)
N_2	0.00(0.00)	0.00(0.00)	0.00(0.00)	100.00(0.00)
ISO/PYR (1:1)				
H_2	0.00(0.00)	0.74(0.02)	16.60(0.72)	82.65(0.74)
N_2	0.00(0.00)	0.00(0.00)	12.34(0.89)	87.64(0.89)
ISO/PYR (5:1)				
H_2	2.25(0.18)	4.56(0.23)	36.03(0.63)	57.15(0.64)
N_2	2.20(0.18)	2.59(0.27)	27.80(1.21)	67.52(1.51)

Reaction conditions: 380°C, 435 cpm, 400 psig H_2 or N_2 charged at ambient conditions.

THP = tetrahydropyrene, HHP = hexahydropyrene, DHP = dihydropyrene, PYR = pyrene.

Numbers in parentheses indicate standard deviations.

Table 4. Product Distributions of Isotetralin with Anthracene or Pyrene for 90 Minute Reactions

Compound/ Conditions	Product Distributions, mole %					
	NAP	1,2-DHN	1,4-DHN	TET	ISO	DEC
ISO/ANT (1:1)						
H_2	79.81(0.59)	5.36(0.30)	0.46(0.05)	12.90(0.30)	0.00(0.00)	1.44(0.03)
N_2	81.53(0.65)	5.45(0.45)	0.40(0.07)	11.18(0.20)	0.00(0.00)	1.42(0.07)
ISO/PYR (5:1)						
H_2	58.07(0.01)	9.12(0.16)	13.91(0.70)	17.73(0.85)	0.00(0.00)	1.13(0.02)
N_2	52.87(0.56)	9.07(0.07)	20.30(0.60)	16.52(0.89)	0.00(0.00)	1.20(0.09)

Reaction conditions: 380°C, 435 cpm, 90 minutes, 400 psig H_2 or N_2 charged at ambient conditions.

ANT = anthracene, PYR = pyrene, NAP = naphthalene, 1,2-DHN = 1,2-dihydronaphthalene, 1,4-DHN = 1,4-dihydronaphthalene, TET = tetralin, ISO = isotetralin, DEC = decalin.

Numbers in parentheses indicate standard deviations.

Table 5. Product Distributions of Isotetralin with Anthracene or Pyrene for 90 Minute Reactions

Product Distributions, mole %				
Compound/ Conditions	OHA	THA	DHA	ANT
ISO/ANT (1:1)				
H_2	0.00(0.00)	6.64(0.31)	75.84(0.82)	17.49(0.61)
N_2	0.00(0.00)	5.23(0.25)	66.18(0.10)	28.57(0.20)
	HHP	THP	DHP	PYR
ISO/PYR (5:1)				
H_2	2.51(0.37)	4.36(0.28)	35.98(0.28)	57.14(0.52)
N_2	2.31(0.16)	3.05(0.33)	30.04(0.76)	64.27(1.24)

Reaction conditions: 380°C, 435 cpm, 90 minutes, 400 psig H_2 or N_2 charged at ambient conditions.

ANT = anthracene, DHA = dihydroanthracene, THA = tetrahydroanthracene, OHA = octahydroanthracene, HHP = hexahydropyrene, THP = tetrahydropyrene, DHP = dihydropyrene, PYR = pyrene, ISO = isotetralin.

Numbers in parentheses indicate standard deviations.

Table 6. Percent Hydrogenation of Aromatics Obtained in Reactions with Hydrogen-Rich Species

Condition	Percent Hydrogenation, %	
	H_2	N_2
HHA/PYR (1:1)	13.59(0.23)	8.14(0.84)
HHA/PYR (5:1)	30.35(0.97)	10.40(2.48)
DHA/PYR (1:1)	2.46(0.18)	1.63(0.85)
DHA/PYR (5:1)	11.27(0.35)	8.58(2.17)
TET/ANT (1:1)	4.53(0.26)	0.25(0.05)
TET/ANT (5:1)	4.45(0.25)	2.64(0.15)
TET/PYR (1:1)	0.00(0.00)	0.00(0.00)
TET/PYR (5:1)	0.41(0.09)	0.16(0.01)
ISO/ANT (1:1)	19.24(0.27)	18.32(0.14)
ISO/ANT (5:1)	24.88(0.07)	24.39(0.18)
ISO/PYR (1:1)	6.02(0.25)	4.11(0.30)
ISO/PYR (5:1)	17.30(0.27)	13.20(0.75)
PHP/ANT (1:1)	3.07(0.27)	0.45(0.17)
PHP/ANT (5:1)	3.97(0.41)	0.60(0.04)

For calculation, octahydroanthracene was considered the most hydrogenated liquid product for anthracene and hexahydropyrene was the most hydrogenated product for pyrene.

Table 7. Percent Hydrogenation of Isotetralin with Anthracene or Pyrene at 30 and 90 Minutes

Time	System	Percent Hydrogenation, %	
		H_2	N_2
30	ISO/ANT (1:1)	19.24(0.27)	18.32(0.14)
90	ISO/ANT (1:1)	22.28(0.12)	19.17(0.08)
30	ISO/PYR (5:1)	17.30(0.27)	13.20(0.75)
90	ISO/PYR (5:1)	17.42(0.50)	14.47(0.63)

Table 8. Product Distributions for Thermal and Catalytic Reactions of Perhydropyrene with Benzophenone at 440°C

Compound/Conditions	Product Distributions, mole %				
	BEN	DPM	PHP	HHP	PYR
PHP/BEN					
N_2 (400 psi) thermal	98.78(0.47)	1.21(0.46)	99.70(0.07)	0.29(0.07)	0.00(0.00)
N_2 (400 psi) catalytic	95.15(1.16)	4.84(1.15)	99.06(0.06)	0.74(0.04)	0.19(0.03)
N_2 (1250 psi) thermal	99.28(0.06)	0.71(0.05)	99.55(0.02)	0.44(0.03)	0.00(0.00)
N_2 (1250 psi) catalytic	94.78(0.15)	5.20(0.15)	98.88(0.10)	0.85(0.07)	0.25(0.04)
H_2 (400 psi) thermal	91.18(0.69)	8.81(0.69)	99.95(0.06)	0.05(0.06)	0.00(0.00)
H_2 (400 psi) catalytic	83.56(0.76)	16.43(0.76)	99.35(0.16)	0.64(0.15)	0.00(0.00)
H_2 (1250 psi) thermal	81.78(0.63)	18.21(0.62)	99.62(0.03)	0.37(0.03)	0.00(0.00)
H_2 (1250 psi) catalytic	69.79(1.27)	30.20(1.27)	99.28(0.03)	0.64(0.03)	0.06(0.01)

Reaction conditions: 440°C, 435 cpm, 400 or 1250 psig H_2 or N_2 charged at ambient conditions.
BEN = benzophenone, DPM = diphenylmethane, PHP = perhydropyrene, HHP = hexahydropyrene, PYR = pyrene.

Table 9. Product Distributions for Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 380°C

Compound/Conditions	ANT	DHA	PHP	HHP	PYR
PHP thermal					
H_2			100.0(0.0)	0.0(0.0)	0.0(0.0)
N_2			100.0(0.0)	0.0(0.0)	0.0(0.0)
PHP 2000 ppm					
H_2			100.0(0.0)	0.0(0.0)	0.0(0.0)
N_2			100.0(0.0)	0.0(0.0)	0.0(0.0)
ANT thermal					
H_2	88.31(1.07)	11.68(1.06)			
N_2	99.53(0.76)	0.47(0.16)			
ANT 2000 ppm					
H_2	83.33(1.50)	16.66(1.50)			
N_2	98.12(0.58)	1.87(0.57)			
PHP/ANT (1:1) thermal					
H_2	87.66(1.10)	12.32(1.10)	99.26(0.73)	0.0(0.0)	0.73(0.78)
N_2	98.16(0.66)	1.82(0.67)	99.22(0.13)	0.0(0.0)	0.77(0.14)
PHP/ANT (1:1) 2000ppm					
H_2	80.65(2.11)	19.33(2.11)	97.20(0.02)	1.92(0.06)	0.86(0.06)
N_2	96.17(0.06)	3.82(0.06)	97.14(0.07)	2.39(0.71)	0.46(0.06)
PHP/ANT (5:1) thermal					
H_2	84.11(1.67)	15.88(1.67)	99.90(0.01)	0.0(0.0)	0.10(0.01)
N_2	97.46(0.81)	2.53(0.82)	98.61(0.17)	0.0(0.0)	1.38(0.18)
PHP/ANT (5:1) 2000ppm					
H_2	55.55(2.41)	44.44(2.41)	99.12(0.12)	0.78(0.11)	0.08(0.01)
N_2	82.36(0.37)	17.64(0.34)	98.85(0.16)	0.95(0.13)	0.19(0.07)

Reaction conditions: 380°C, 435 cpm, 400 psig H_2 or N_2 charged at ambient conditions. Reactions were performed thermally and catalytically.
Catalytic reactions contained 2000 ppm of sulfur introduced as thiophenol.
ANT = anthracene, DHA = dihydroanthracene, HHP = hexahydropyrene, PYR = pyrene, HHP = hexahydropyrene.
Numbers in parentheses represent standard deviations.

Table 10. Product Distributions for Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 440°C

Compound/Conditions	ANT	DHA	THA	OHA	PHP	HHP	PYR
PHP thermal							
H_2					100.0(0.0)	0.0(0.0)	0.0(0.0)
N_2					100.0(0.0)	0.0(0.0)	0.0(0.0)
PHP 2000 ppm							
H_2					100.0(0.0)	0.0(0.0)	0.0(0.0)
N_2					100.0(0.0)	0.0(0.0)	0.0(0.0)
ANT thermal							
H_2	43.50(0.78)	54.04(0.84)	1.11(0.05)	1.32(0.03)			
N_2	99.32(0.08)	0.67(0.08)	0.0(0.0)	0.0(0.0)			
ANT 2000 ppm							
H_2	39.28(1.34)	57.50(1.25)	2.23(0.08)	0.97(0.0)			
N_2	98.50(0.14)	1.49(0.14)	0.0(0.0)	0.0(0.0)			
PHP/ANT (1:1) thermal							
H_2	37.97(2.68)	61.76(2.56)			98.96(0.62)	0.95(0.69)	0.08(0.16)
N_2	98.79(0.17)	1.19(0.17)			98.20(0.29)	0.79(0.15)	1.00(0.22)
PHP/ANT (1:1) 2000 ppm							
H_2	40.29(0.77)	59.70(0.76)			97.31(0.16)	2.67(0.16)	0.00(0.00)
N_2	94.07(0.17)	5.91(0.50)			97.84(0.91)	1.69(0.58)	0.45(0.53)
PHP/ANT (5:1) thermal							
H_2	38.12(0.65)	61.87(0.65)			99.48(0.11)	0.45(0.12)	0.05(0.01)
N_2	89.57(0.76)	10.41(0.76)			99.37(0.10)	0.55(0.07)	0.07(0.05)
PHP/ANT (5:1) 2000 ppm							
H_2	41.95(1.29)	58.04(1.30)			99.44(0.05)	0.51(0.02)	0.04(0.03)
N_2	86.99(0.91)	13.00(0.90)			99.05(0.19)	0.80(0.19)	0.14(0.01)

Reaction conditions: 440°C, 435 cpm, 400 psig H_2 or N_2 charged at ambient conditions. Reactions were performed thermally and catalytically.
Catalytic reactions contained 2000 ppm sulfur introduced as thiophenol.
ANT = anthracene, DHA = dihydroanthracene, THA = tetrahydroanthracene, OHA = octahydroanthracene, PHP = perhydropyrene, HHP = hexahydropyrene, PYR = pyrene
Numbers in parentheses represent standard deviations.

Table 11. Definitions of Calculated Terms

Percent Hydrogenation

Moles of hydrogen required to achieve the liquid products as a percentage of the moles of hydrogen needed to produce the most hydrogenated product.

Calculation of Moles of Hydrogen Used by a Hydrogen Acceptor

(Moles of hydrogen accepted by the hydrogen acceptor) = (moles of product x moles of hydrogen used)

Calculation of Moles of Hydrogen Released from Hydrogen Donor

(Moles of hydrogen released from the hydrogen donor) = (hydrogen released from the hydrogen donor - hydrogen used by the hydrogen donor) = (moles of product x moles of hydrogen released) - (moles of product x moles of hydrogen used)

Calculation of Hydrogen Efficiency

Hydrogen efficiency = (moles of hydrogen accepted by the hydrogen acceptor) divided by (moles of hydrogen released by the hydrogen donor)

Calculation of the Amount of Gaseous Hydrogen that was Accepted by Hydrogen Acceptor

I. Amount of hydrogen accepted that came from gaseous hydrogen = moles of hydrogen accepted by hydrogen acceptor - moles of hydrogen released from the donor.

II. Amount of hydrogen accepted that came from gaseous hydrogen = moles of hydrogen accepted by hydrogen acceptor under a hydrogen atmosphere - moles of hydrogen accepted by hydrogen acceptor under a nitrogen atmosphere.

Table 12. Percent Hydrogenation of Thermal and Catalytic Reactions of Perhydropyrene with Anthracene

	H_2	N_2
380°C Thermal		
PHP/ANT (1:1)	3.08(0.28)	0.46(0.17)
PHP/ANT (5:1)	3.97(0.42)	0.63(0.02)
380°C Catalytic		
PHP/ANT (1:1)	4.83(0.53)	0.96(0.14)
PHP/ANT (5:1)	11.11(0.60)	4.40(0.09)
440°C Thermal		
PHP/ANT (1:1)	15.44(0.64)	0.30(0.04)
PHP/ANT (5:1)	15.47(0.16)	2.60(0.19)
440°C Catalytic		
PHP/ANT (1:1)	14.93(0.19)	1.48(0.13)
PHP/ANT (5:1)	14.51(0.33)	3.25(0.22)

PHP = Perhydropyrene ANT = Anthracene

Table 13. Moles of Hydrogen Released from the Hydrogen Donor

	Moles of Hydrogen Released x 10^4	
	H_2 Atmosphere	N_2 Atmosphere
380°C Thermal		
PHP/ANT (1:1)	0.27(0.02)	0.28(0.05)
PHP/ANT (5:1)	0.18(0.01)	0.25(0.02)
380°C Catalytic		
PHP/ANT (1:1)	0.75(0.01)	0.71(0.16)
PHP/ANT (5:1)	1.05(0.14)	1.44(0.22)
440°C Thermal		
PHP/ANT (1:1)	0.24(0.13)	0.55(0.09)
PHP/ANT (5:1)	0.61(0.13)	0.77(0.15)
440°C Catalytic		
PHP/ANT (1:1)	0.61(0.03)	0.55(0.27)
PHP/ANT (5:1)	0.67(0.08)	1.18(0.22)

PHP = perhydropyrene ANT = anthracene

Table 14. Moles of Hydrogen Accepted by the Hydrogen Acceptor

	Moles of Hydrogen Released x 10^4	
	H_2 Atmosphere	N_2 Atmosphere
380°C Thermal		
PHP/ANT (1:1)	0.69(0.05)	0.10(0.03)
PHP/ANT (5:1)	0.88(0.09)	0.14(0.00)
380°C Catalytic		
PHP/ANT (1:1)	1.09(0.11)	0.21(0.03)
PHP/ANT (5:1)	2.49(0.13)	1.00(0.00)
440°C Thermal		
PHP/ANT (1:1)	3.46(0.14)	0.06(0.00)
PHP/ANT (5:1)	3.46(0.03)	0.58(0.04)
440°C Catalytic		
PHP/ANT (1:1)	3.34(0.07)	0.33(0.02)
PHP/ANT (5:1)	3.27(0.09)	0.72(0.05)

PHP = perhydropyrene ANT = anthracene

Table 15. Hydrogen Efficiency

	Hydrogen Efficiency	
	H_2 Atmosphere	N_2 Atmosphere
380°C Thermal		
PHP/ANT (1:1)	2.57(0.22)	0.35(0.09)
PHP/ANT (5:1)	4.91(0.84)	0.57(0.07)
380°C Catalytic		
PHP/ANT (1:1)	1.44(0.18)	0.31(0.91)
PHP/ANT (5:1)	2.38(0.28)	0.70(0.12)
440°C Thermal		
PHP/ANT (1:1)	19.31(14.13)	0.13(0.04)
PHP/ANT (5:1)	5.88(1.27)	0.78(0.15)
440°C Catalytic		
PHP/ANT (1:1)	5.48(0.30)	0.77(0.49)
PHP/ANT (5:1)	4.91(0.55)	0.64(0.17)

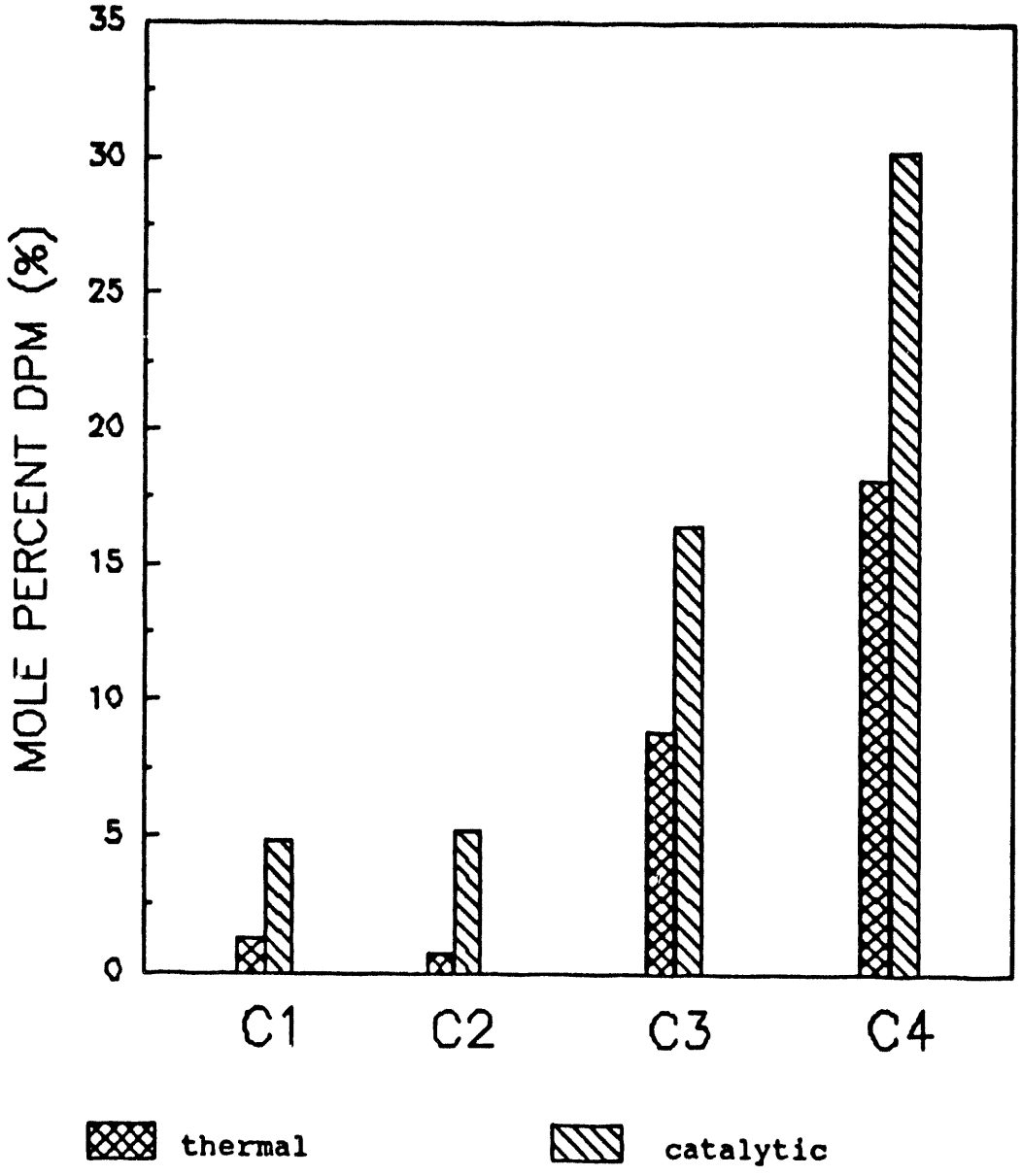
PHP = perhydropyrene ANT = anthracene

$$\text{Hydrogen efficiency} = \frac{\text{moles of hydrogen used by the hydrogen acceptor}}{\text{moles of hydrogen released by the hydrogen donor}}$$

Table 16. Moles of Hydrogen from Gaseous Hydrogen

	Definition 1 (moles x 10^4) H_2	Definition 2 (moles x 10^4) H_2
380°C Thermal		
PHP/ANT (1:1)	0.41(0.05)	0.59(0.08)
PHP/ANT (5:1)	0.70(0.10)	0.74(0.09)
380°C Catalytic		
PHP/ANT (1:1)	0.32(0.12)	0.88(0.14)
PHP/ANT (5:1)	1.43(0.12)	1.49(0.13)
440°C Thermal		
PHP/ANT (1:1)	3.21(0.27)	3.40(0.14)
PHP/ANT (5:1)	2.85(0.13)	2.88(0.07)
440°C Catalytic		
PHP/ANT (1:1)	2.73(0.03)	3.01(0.09)
PHP/ANT (5:1)	2.58(0.04)	2.55(0.14)

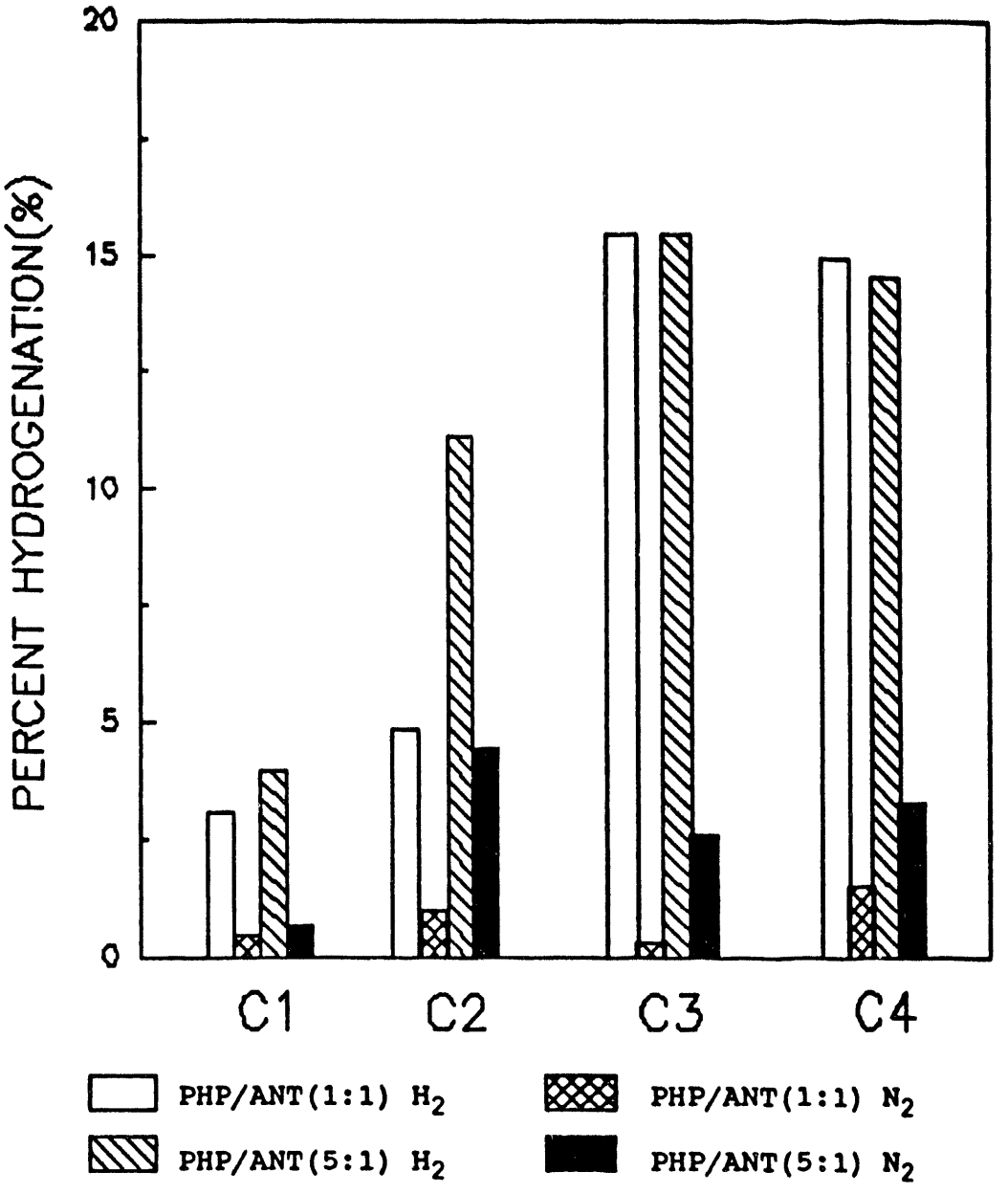
PHP = perhydropyrene ANT = anthracene



C1= N_2 400 psi
C3= H_2 440 psi

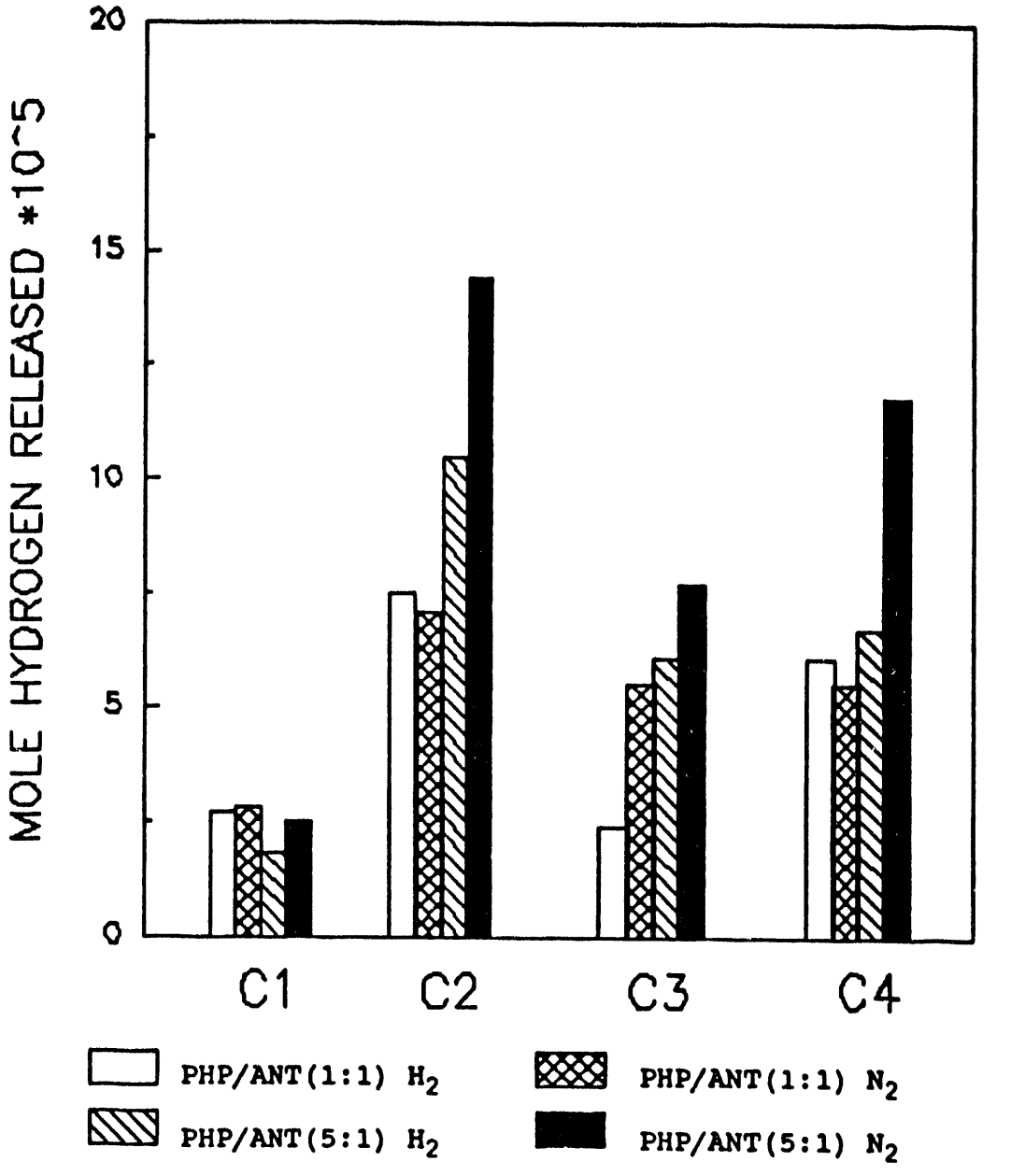
C2= N_2 1250 psi
C4= H_2 1250 psi

Figure 1. Mole Percent of Diphenylmethane Produced from Thermal and Catalytic Reactions of Perhydropyrene/Benzophenone



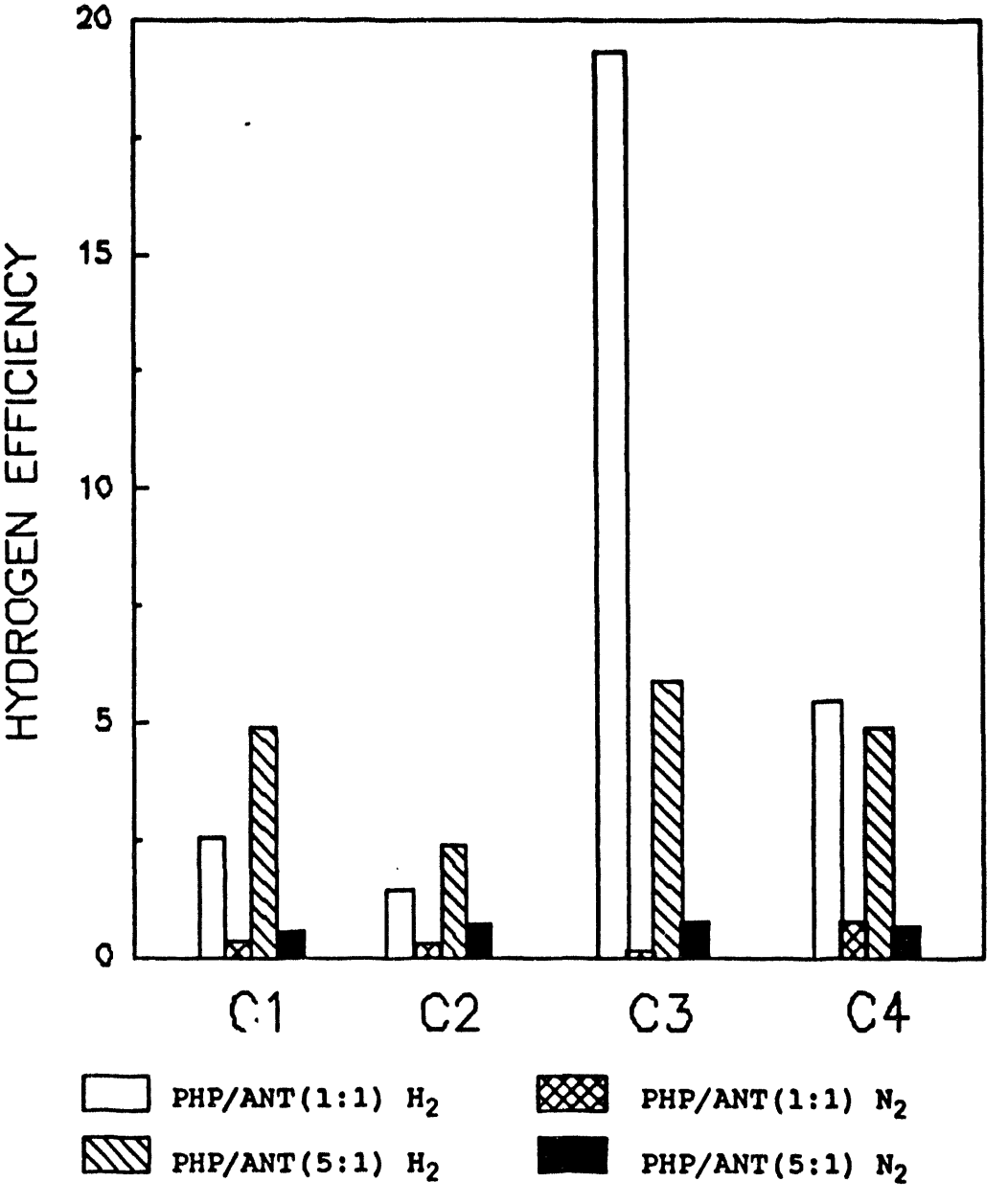
C1= PHP/ANT 380°C thermal
C2= PHP/ANT 380°C catalytic
C3= PHP/ANT 440°C thermal
C4= PHP/ANT 440°C catalytic

Figure 2. Percent Hydrogenation of Thermal and Catalytic Reactions of Perhydropyrene with Anthracene



C1= PHP/ANT 380°C thermal
C2= PHP/ANT 380°C catalytic
C3= PHP/ANT 440°C thermal
C4= PHP/ANT 440°C catalytic

Figure 3. Moles of Hydrogen Released by Hydrogen Donor during Thermal and Catalytic Reactions of Perhydropyrene with Anthracene



C1= PHP/ANT 380°C thermal
C2= PHP/ANT 380°C catalytic
C3= PHP/ANT 440°C thermal
C4= PHP/ANT 440°C catalytic

Figure 4. Hydrogen Efficiency of Thermal and Catalytic Reactions of Perhydropyrene with Anthracene

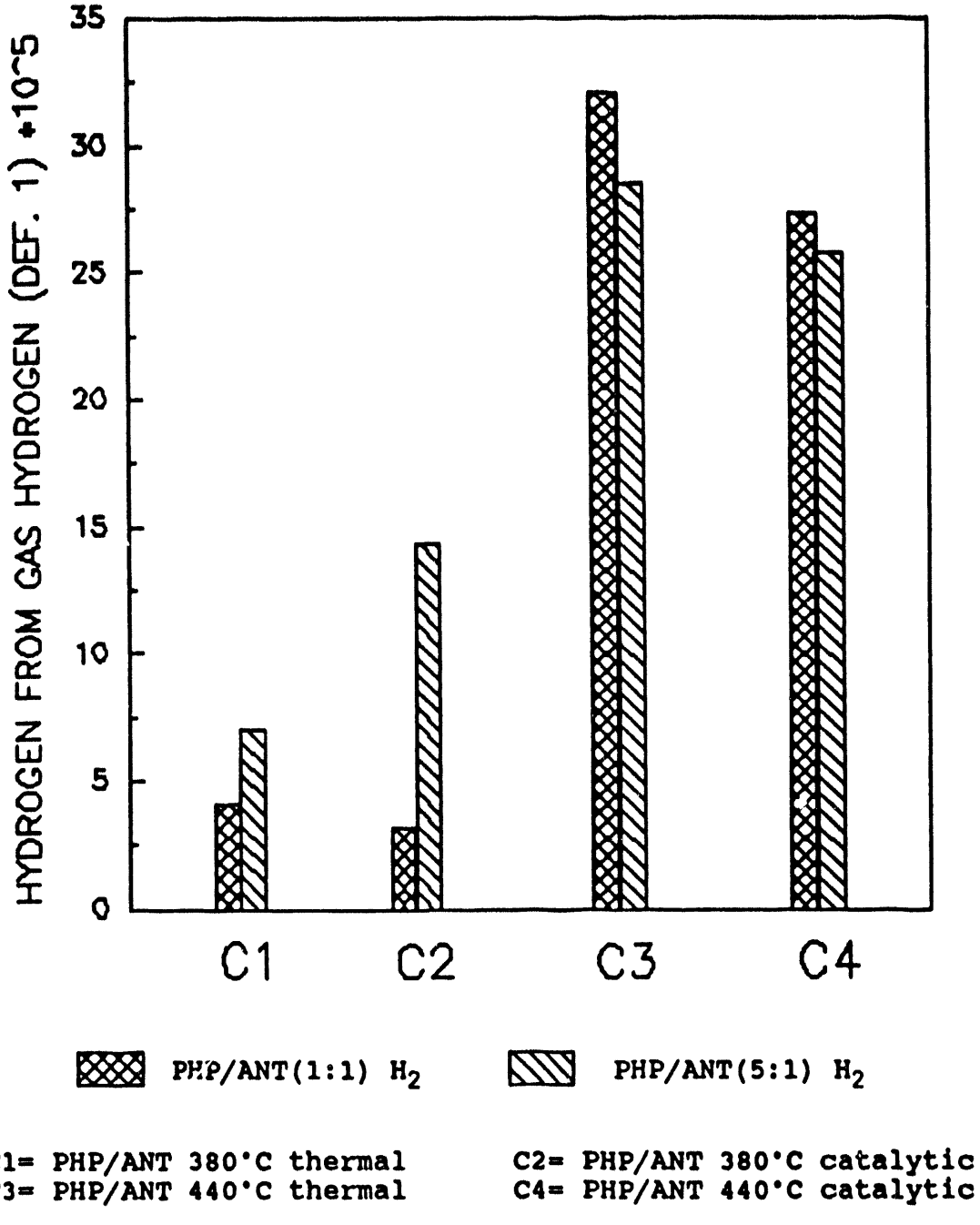


Figure 5: Hydrogen which came from Gaseous Hydrogen in Thermal and Catalytic Reactions of Perkydropyrene with Authiacene (definition one)

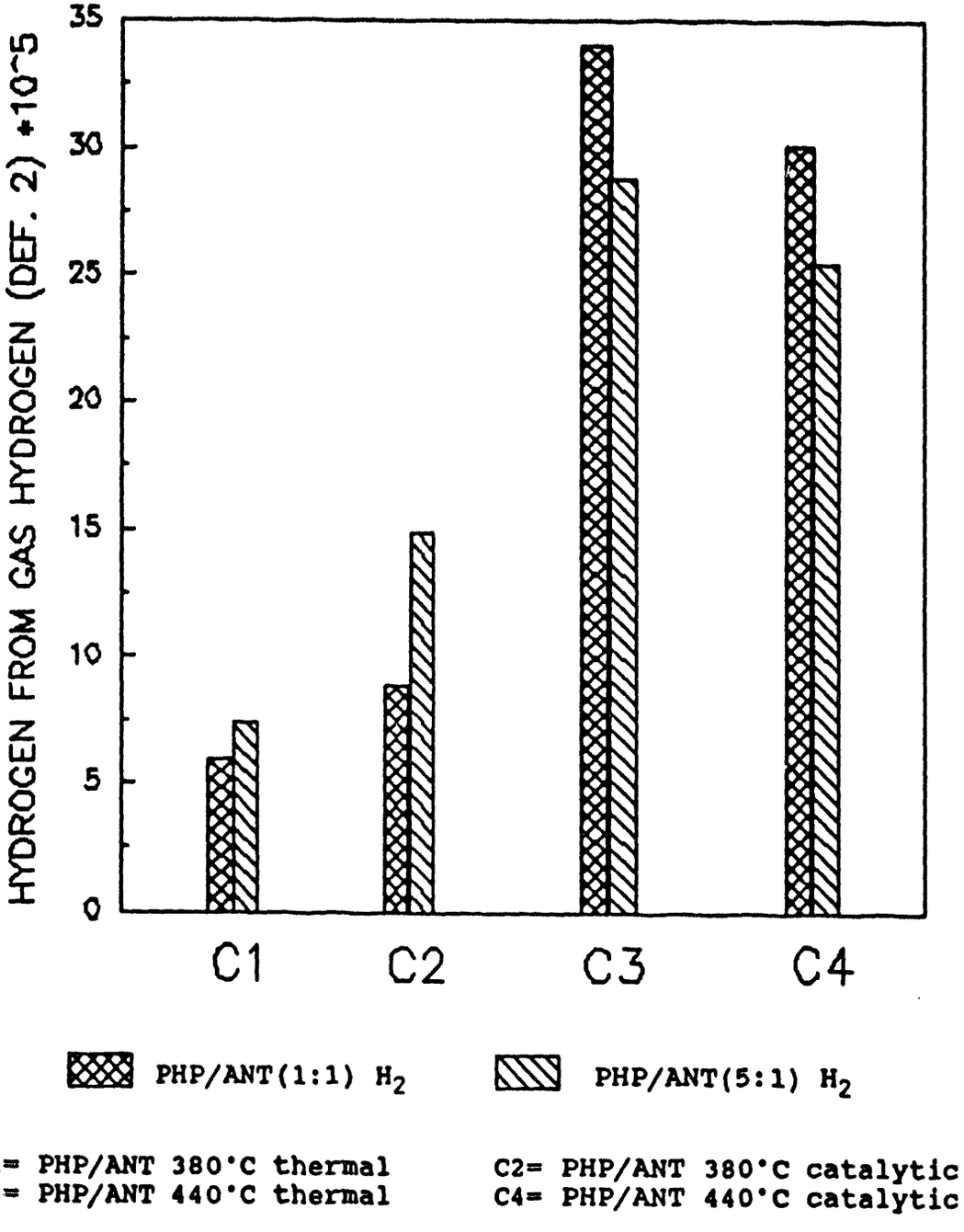


Figure 6: Hydrogen which came from Gaseous Hydrogen in Thermal and Catalytic Reactions of Perkydropyrene with Authracene (definition two).

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