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INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION

Quarterly Report for
July-September, 1976

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ABSTRACT

In this quarterly report, the initial stages of research in the study of hydrogen transfer in coal hydrogenation are described. Preliminary experiments in the transfer of hydrogen from a donor tetralin, to a potential acceptor, phenanthrene, have been completed. The amount of transfer was low, but interesting side reactions were observed. The procurement of tagged compounds and the evaluation of analytical test procedures is progressing on schedule. Plans called for the use of asymmetric octahydrophenanthrene as one of the model donor compounds, but it has been replaced with the symmetric isomer due to stability considerations.

OBJECTIVE AND SCOPE OF WORK

The overall objective of this study is to develop an understanding of the mechanism of hydrogen transfer to coal during coal liquefaction. This will be done by the use of tagged compounds as donors and acceptors. The tagged compounds will include those containing stable (C^{13} and deuterium) or radioactive isotopes (C^{14} and H^3) or those having functionality that allows for isolation by extraction (tetrahydroquinoline). Experimentation will be conducted at conditions consistent with processes currently being developed to convert coal to liquids.

The project is divided into two phases, the first dealing with the study of model compounds, the second consisting of the application of these results to the study of coal and coal derived liquids. The following is a summary of the tasks to be covered in the initial phase of this project:

Phase I. Model Compound Investigation (18 months)
Stage 1. Preparative Work (6 months)

a. Establish an inventory of model compounds including donors and acceptors such as tetralin, phenanthrene, octahydrophenanthrene, and coal derived aromatics containing heteroatoms. Compounds containing the above-mentioned tags will also be purchased or synthesized.

b. Select appropriate methods for the analysis of feed and product streams.

c. Conduct preliminary experimentation and establish optimum plans for the continuing program. These experiments will be made to test analytical procedures, confirm tracer and material balances, and determine the extent of reactions between various donors and acceptors.

d. Submit a report on the above and set up a plan for subsequent experimentation.

SUMMARY OF PROGRESS TO DATE

The project is progressing according to schedule. An inventory of model compounds is being established. Suppliers have been found for the commercially available donor and acceptor model compounds. The synthesis of tagged compounds is also underway. The first series of preliminary hydrogen transfer experiments has been completed. It was shown that only a low level of transfer occurs between aromatic species, namely tetralin to phenanthrene. During these latter runs, analysis of the feed and product streams was made using gas and liquid chromatography along with mass spectrometry of isolated samples prepared by the LC. As anticipated, more work is needed in this latter area, and it appears to be progressing on schedule.

A copy of the program schedule is included as Figure 1.

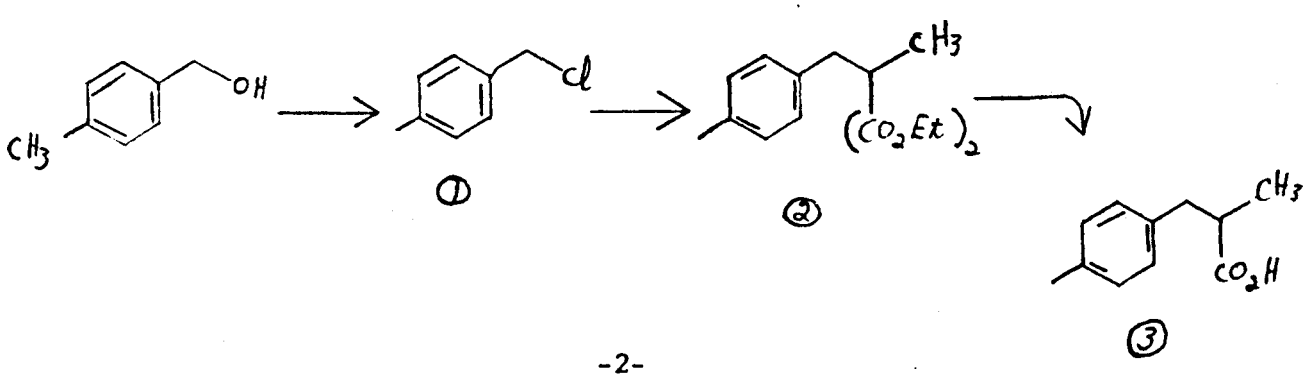
DETAILED DESCRIPTION OF TECHNICAL PROGRESS

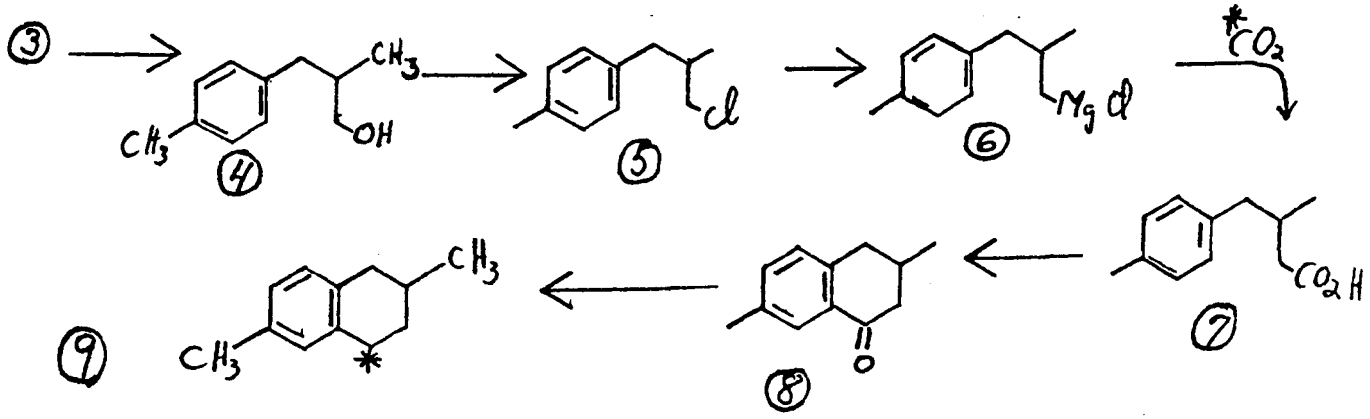
Stage 1. Preparative Work

a. With respect to establishing an inventory of model compounds, suppliers have been found for the commercially available donor and acceptor compounds. The following compounds are on-hand: tetralin, phenanthrene, bibenzyl, N-ethylcarbazole, dibenzofuran, dibenzothiophene, α-tetralone, and dibenzyl ether. Several additional acceptors are being considered and they will be ordered shortly.

As part of this area, donor solvents with C^{13} labels in specific positions are being prepared. This synthesis is being conducted in collaboration with Professor E. J. Eisenbraun of Oklahoma State University. The specific donors with unique structures and excellent donor capabilities are 2,6-dimethyltetralin and octahydrophenanthrene. In the former, the alkyl groups on both the aromatic and hydroaromatic rings may show an interesting effect on hydrogen transfer, particularly when compared to tetralin. The second compound offers a high level of hydroaromatics and the possibility of ring opening as a side reaction.

Considering the ease and number of synthesis steps, the decision has been made to prepare 2,6-dimethyl-$4C^{13}$-tetralin first. The planned synthesis route is represented as follows:



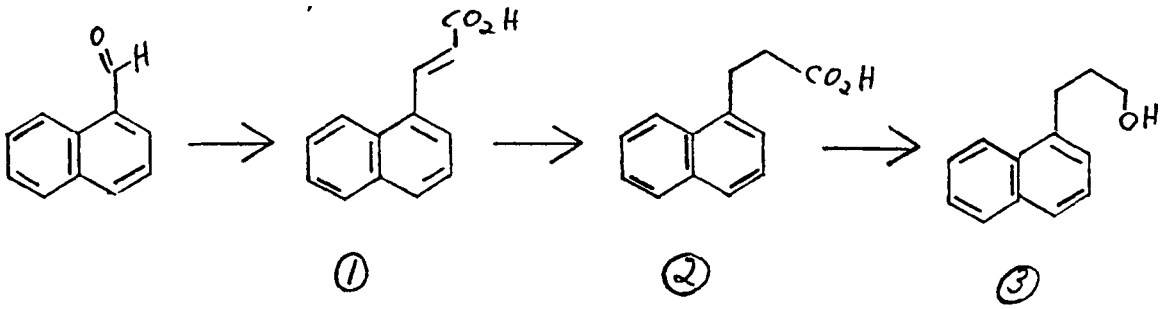


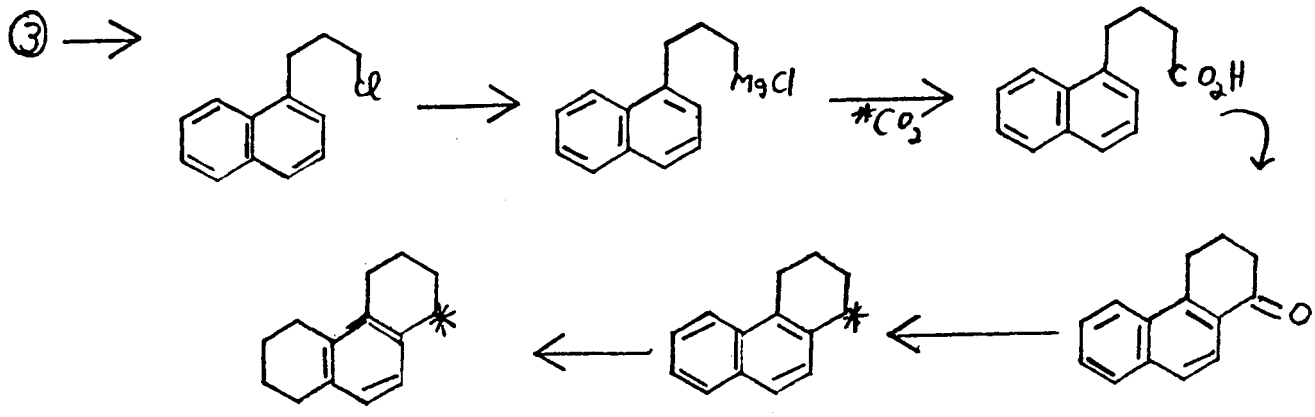
Details for performing the synthesis in high yield are currently being developed. Yields of reactions for compounds up through number 6 appear to be in excess of 90%. Before using the expensive $^{13}CO_2$ to produce compound number 7, experience will be gained using "cold" CO_2. Barium carbonate will be used as the source of CO_2, and the labeled salt is now on order. Since this synthesis route is novel, particular care is being taken to establish the structure of each intermediate, including the use of ^{13}C NMR.

The second compound, octahydrophenanthrene, exists as either the symmetric or asymmetric isomer, as shown below:

Since the symmetric isomer is commercially available and it is a primary product from the hydrogenation of phenanthrene, its use as an excellent donor solvent has been demonstrated in our laboratory. The asymmetric isomer is not as common, but its structure suggests that it would serve as a good donor solvent. In addition, it can be synthesized in high purity and be made with a ^{13}C label at position C-10. Consideration of the latter asymmetric derivative as a model solvent was given. However, as noted below (a'), preliminary experiments demonstrated that this latter compound was not sufficiently stable at reaction conditions.

Considering the above, we are now exploring routes to synthesize the symmetric isomer and place a ^{13}C label in a hydroaromatic ring. One direct route being pursued is as follows:





Although this synthesis has never been reported in the literature, all steps are predicted to be in high yield. All chemicals have been ordered and initial steps taken.

With further reference to preparing tagged compounds, a cylinder of deuterium is on-hand. It will be used in preparing deuterated tetralin for subsequent experimentation.

a'. Since octahydrophenanthrene is planned to be used as one of the tagged donor solvents, a qualitative evaluation of its two isomers for both thermal stability and coal solvation was made. In agreement with earlier observations[1], the symmetric isomer was completely stable when held in a heated autoclave at 427°C (800°F) for 60 minutes. Greater than 95% recovery of unchanged solvent was observed.

The asymmetric isomer was tested at the same operating conditions. This compound was found unstable as demonstrated by a rapid pressure increase. Analysis of the liquid product indicated that essentially all of the starting compound was lost and about 50% cracked to compounds having less than 12 carbons. The remaining component was symmetric octahydrophenanthrene. For reference, a copy of the gas chromatographic results are attached as Figure 2.

When each of the above isomers was used as solvent for the liquefaction of Big Horn, WY, sub-bituminous coal, greater than 90% MAF solvation was observed. (Run conditions were: 427°C, 60 minutes, 3.4 MPa (500 psig) initial pressure, and a solvent to coal ratio of 3 to 1). Surprisingly, the asymmetric isomers did not undergo extensive decomposition to low molecular weight species. This implies that the hydrogen transfer to the dissolving coal proceeded faster than the thermal cracking of the solvent.

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[1]R. G. Ruberto, D. C. Cronauer, D. M. Jewell, and K. S. Seshadri, "Structural Aspects of Sub-bituminous Coal Deduced from Solvation Studies: II Hydrophenanthrene Solvents," accepted for publication in Fuel.

b. In the testing of analytical methods, initial efforts are being directed toward standardization and calibration of both gas-liquid chromatography (GLC) and liquid chromatography (LC). High resolution capillary GLC using a 100 foot SCOT column appears to offer sufficient separation of our mixtures. A reference LC scan of anticipated products from tetralin-phenanthrene reactions is shown in Figure 3.

While the high resolution of the capillary GLC is desirable, problems can occur in that isolation of isomers can be accomplished. The identification of these individual peaks is difficult due to the lack of availability of pure reference compounds. Medium resolution GC in which packed columns are used is being interfaced with a mass spectrometer (Du Pont 21-491). This combination of analytical tools should provide the needed separation and peak identification.

A high performance liquid chromatographic instrument is being evaluated in both analytical and preparative modes. This apparatus primarily separates groups or classes of compounds. It can be used in conjunction with refractive index, ultraviolet, NMR, and mass spectroscopy. Calibration is underway for mixtures of decalin, naphthalene, tetralin, phenanthrene, and the various hydrophenanthrenes. An example of an LC scan for such a mixture is shown in Figure 4.

c. Three series of preliminary experiments have been made with mixtures of tetralin and phenanthrene (donor and acceptor, respectively). These runs were made in a flow-through micro-reactor consisting of an 8 mm (5/16") ID by 89 cm (35") length tube packed with 10 by 40 mesh quartz chips. The first series (917) was made with tetralin at temperatures between 425° and 475°C and nominal residence times of 105 and 210 minutes. The second series (918) was made in a similar manner using a feed mixture of 20 wt.% phenanthrene in tetralin. The final series was made at a high temperature (475°C) and long residence time with feed that contained 0, 1, 5, 10, and 20 wt.% phenanthrene. Reaction conditions and results of the above experiments are listed in Table I.

It is noted that the tetralin used in these preliminary experiments was a "purified" grade that even after distillation contained appreciable levels of decalin (0.3 wt.%) and naphthalene (3.0%). Due to the presence of impurities and the existence of some unresolved GLC peaks in tetralin and its reaction products with phenanthrene, the following definition of conversion is used in the discussion of results:

$$\% \text{ Conversion} = \frac{\% \text{ in Feed} - \% \text{ in Product}}{\% \text{ in Feed}} \times 100$$

The first series of experiments was made with the above tetralin to test its stability at reaction conditions. Conversion of tetralin to by-products was low (ca. 0.5%) at reactor conditions of 425° and 450°C and a nominal residence time of 105 minutes. With a temperature increase to

475°C conversion increased to 2.3%. Essentially this same level was observed when the nominal residence time was decreased to 55 minutes at 475°C.

Unexpected results were observed in the second experimental series (918) made with 20% phenanthrene. Tetralin conversions were 6-10 times greater than those of the preceding series, namely 3.5% at 425°C up to 2.3% at 475°C. However, this change could not be accounted for in a transfer of hydrogen to phenanthrene. Considering that the feed phenanthrene concentration was one-fourth that of tetralin and only 8 to 12% conversion of phenanthrene was observed, tetralin must have been reacting with itself. It appears that the phenanthrene had a "catalytic effect" on this latter tetralin reaction. This effect of phenanthrene upon the tetralin conversion over the temperature range is shown in Figure 5.

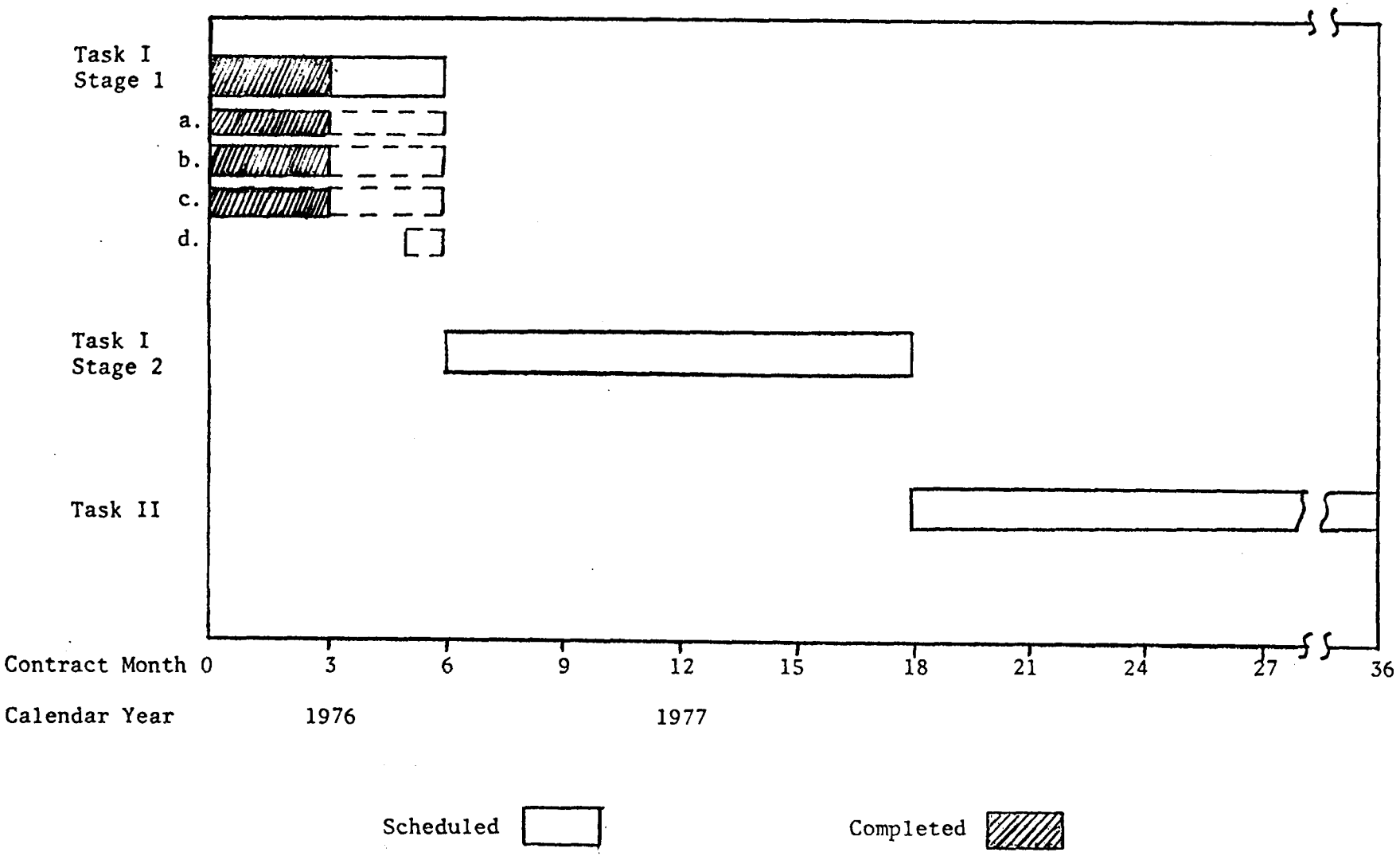
In further confirmation, results of the 919 series show that as little as 1% phenanthrene in the feed increased tetralin conversion. As noted in Figure 6, this conversion appeared to level out at about 5% phenanthrene.

The above has been described as tetralin conversion, but a confirmed product analysis has not been established. Typically, the decreases in tetralin have been offset by increases in components that were showing up in GLC where decalin and naphthalene were expected based on standards. However, LC analysis has not confirmed these results.

Due to the intended future use of tetralin and substituted derivatives, further testing of analytical procedures for the above reaction is continuing. In addition, experiments are going to be made with the above listed (Ia) acceptors in combination with tetralin.

Figure 1

Program Schedule for Hydrogen Transfer Project



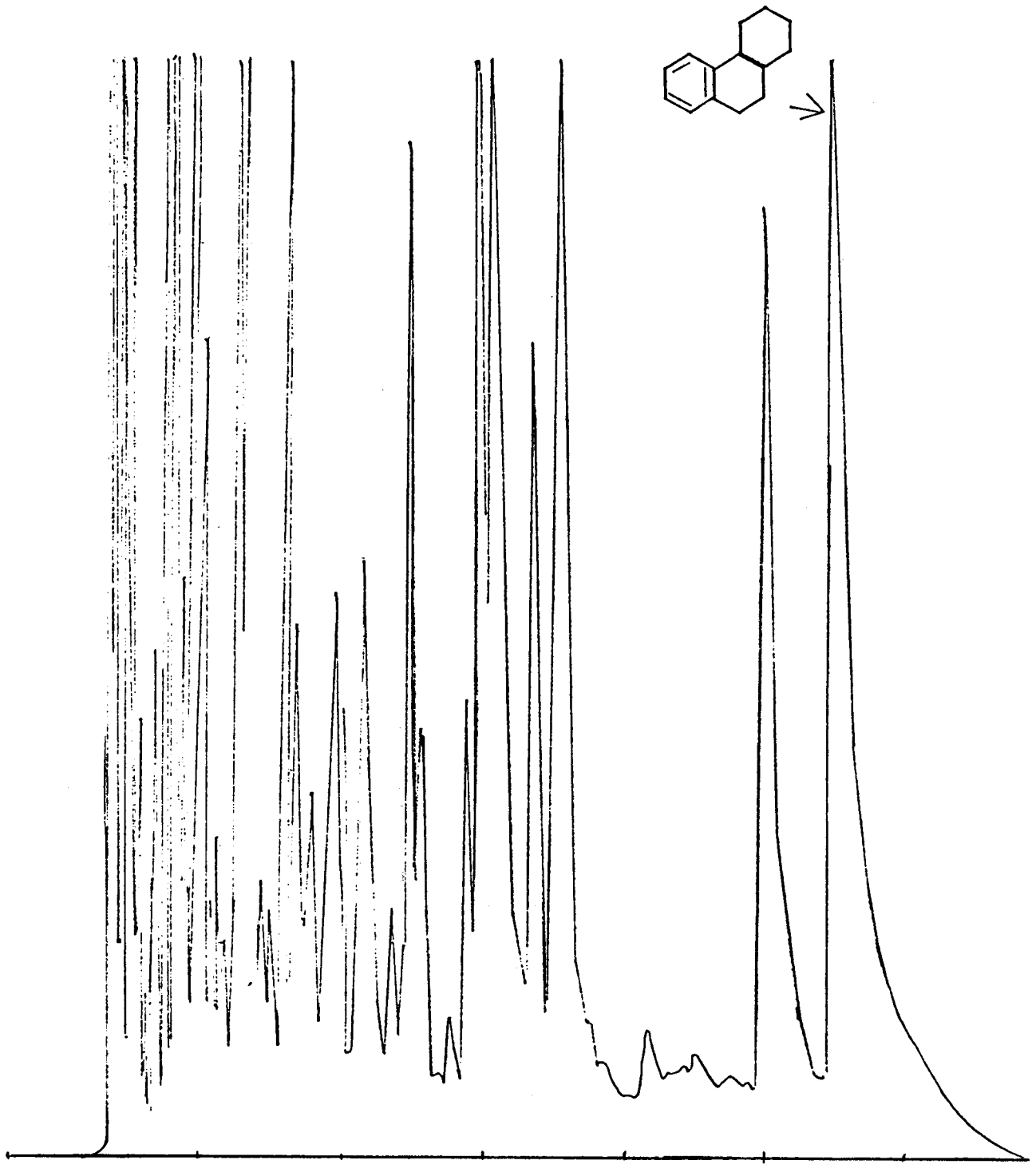


Figure 2

High Resolution GLC of Thermally Treated asyn-Octahydrophenanthrene

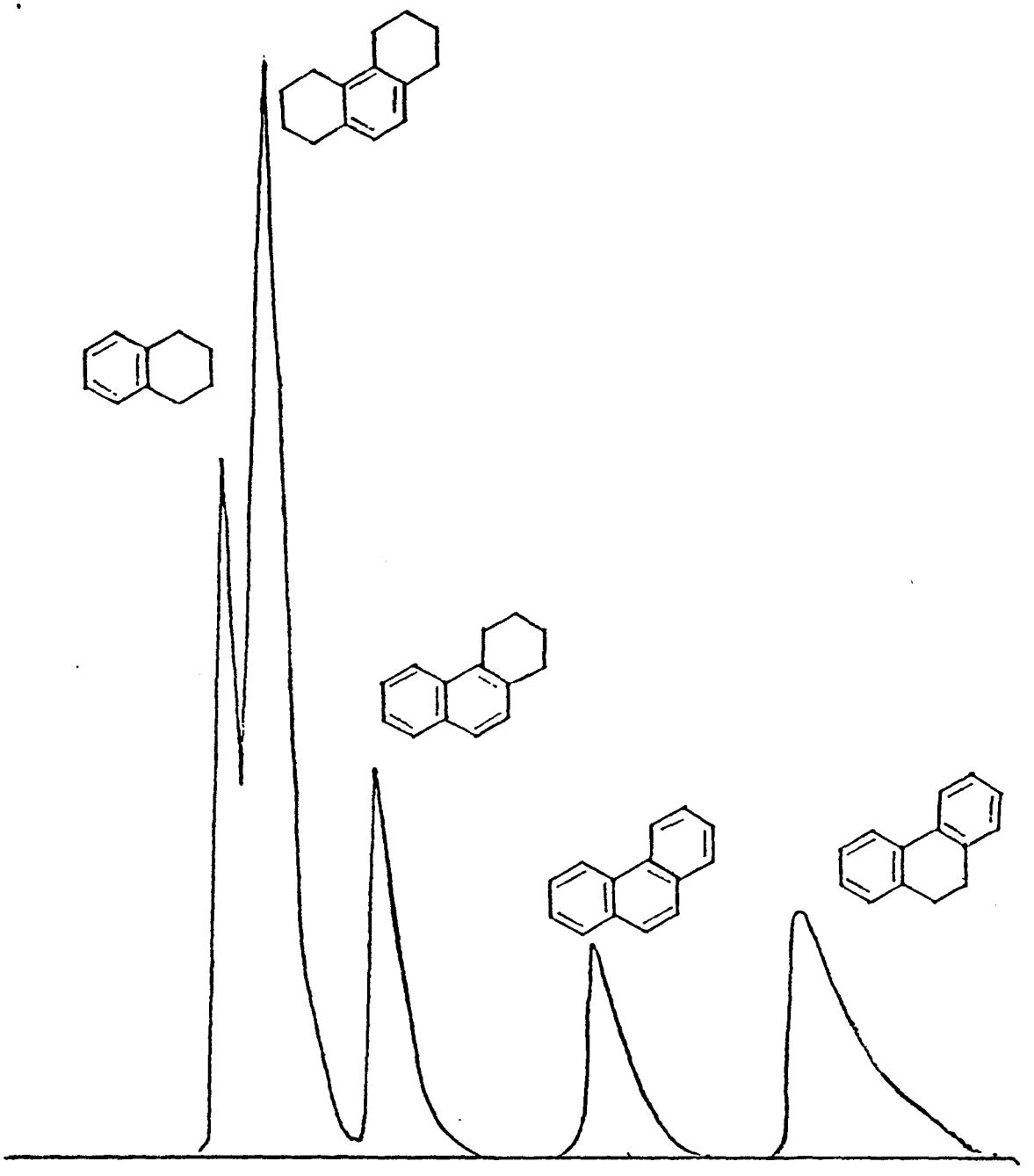


Figure 3

HPLC Separation of Aromatic Standards

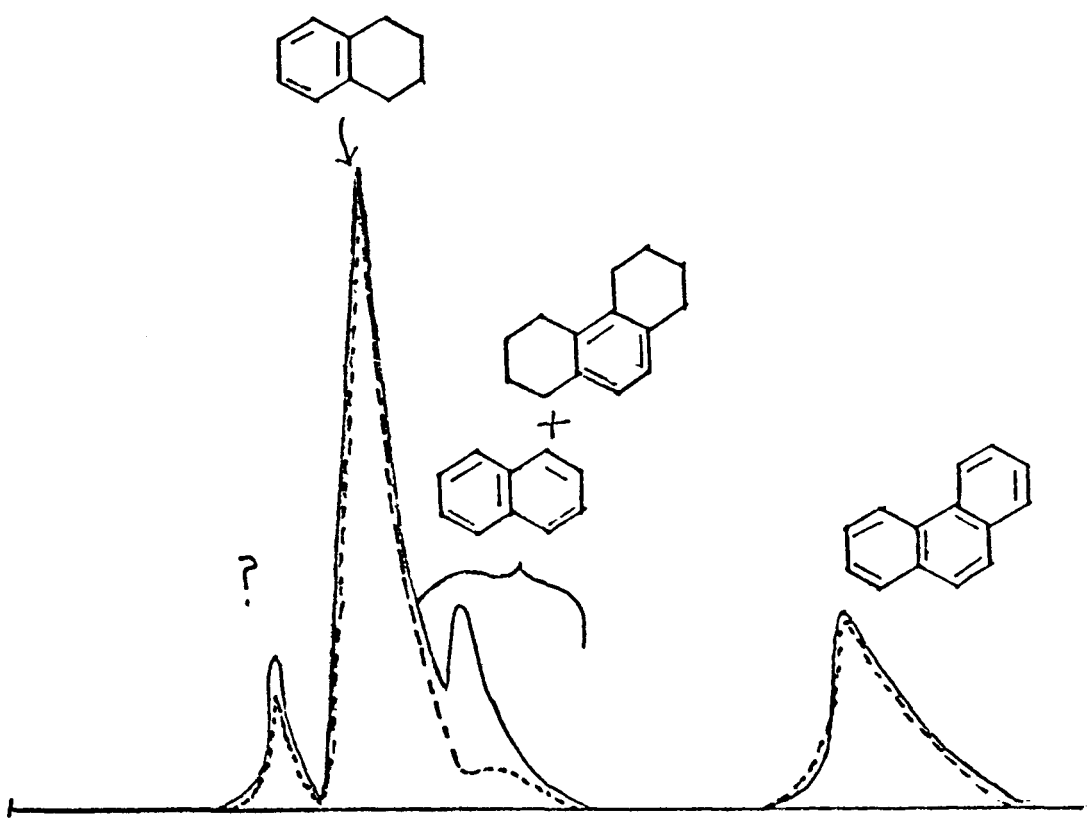


Figure 4

HPLC of Tetralin-Phenanthrene (80:20) before (—)
and after (---) Reaction at 475°C

Figure 5

Tetralin Conversion as Functions
of Temperature and Phenanthrene Level

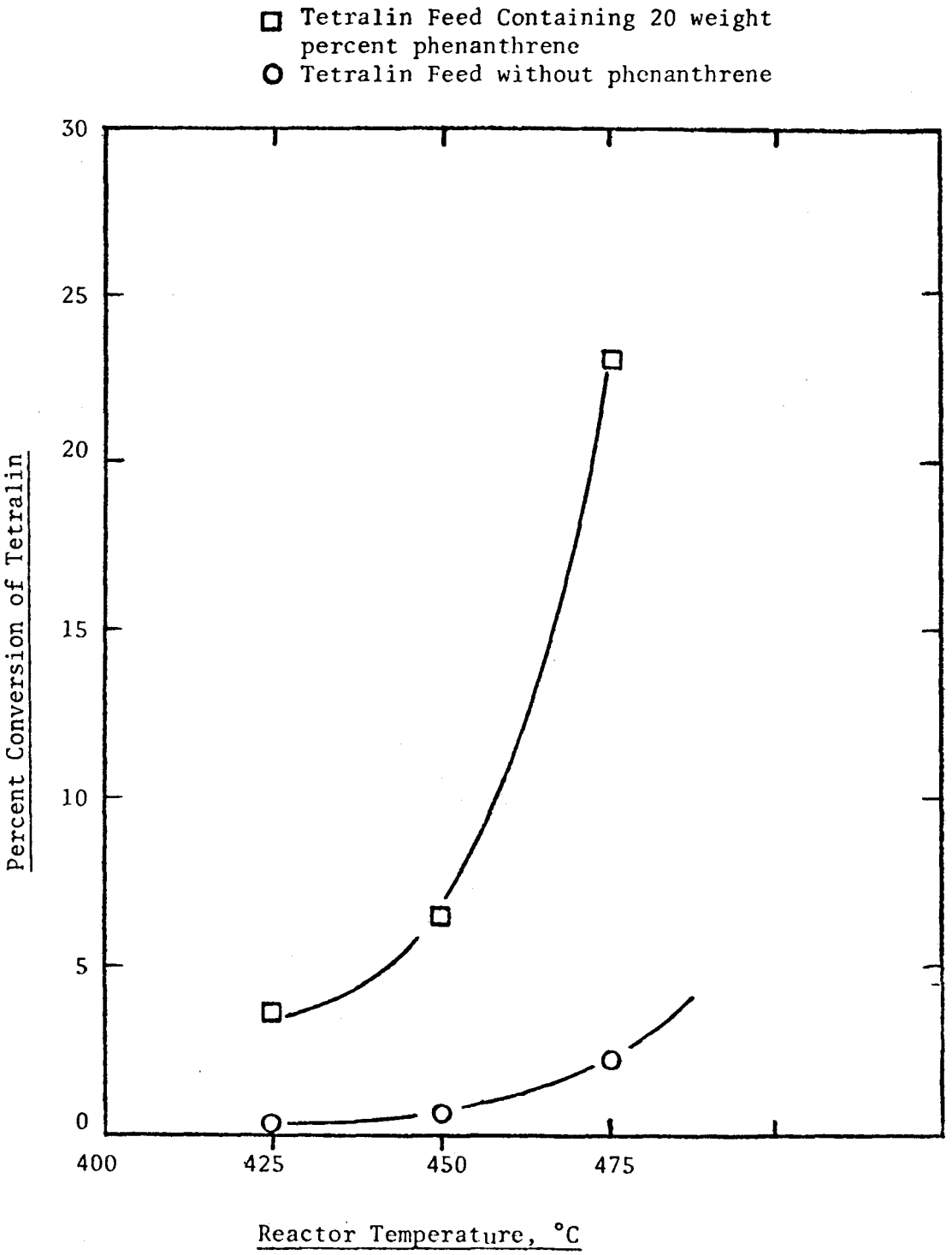


Figure 6

Effect of Phenanthrene Concentration upon Tetralin Conversion

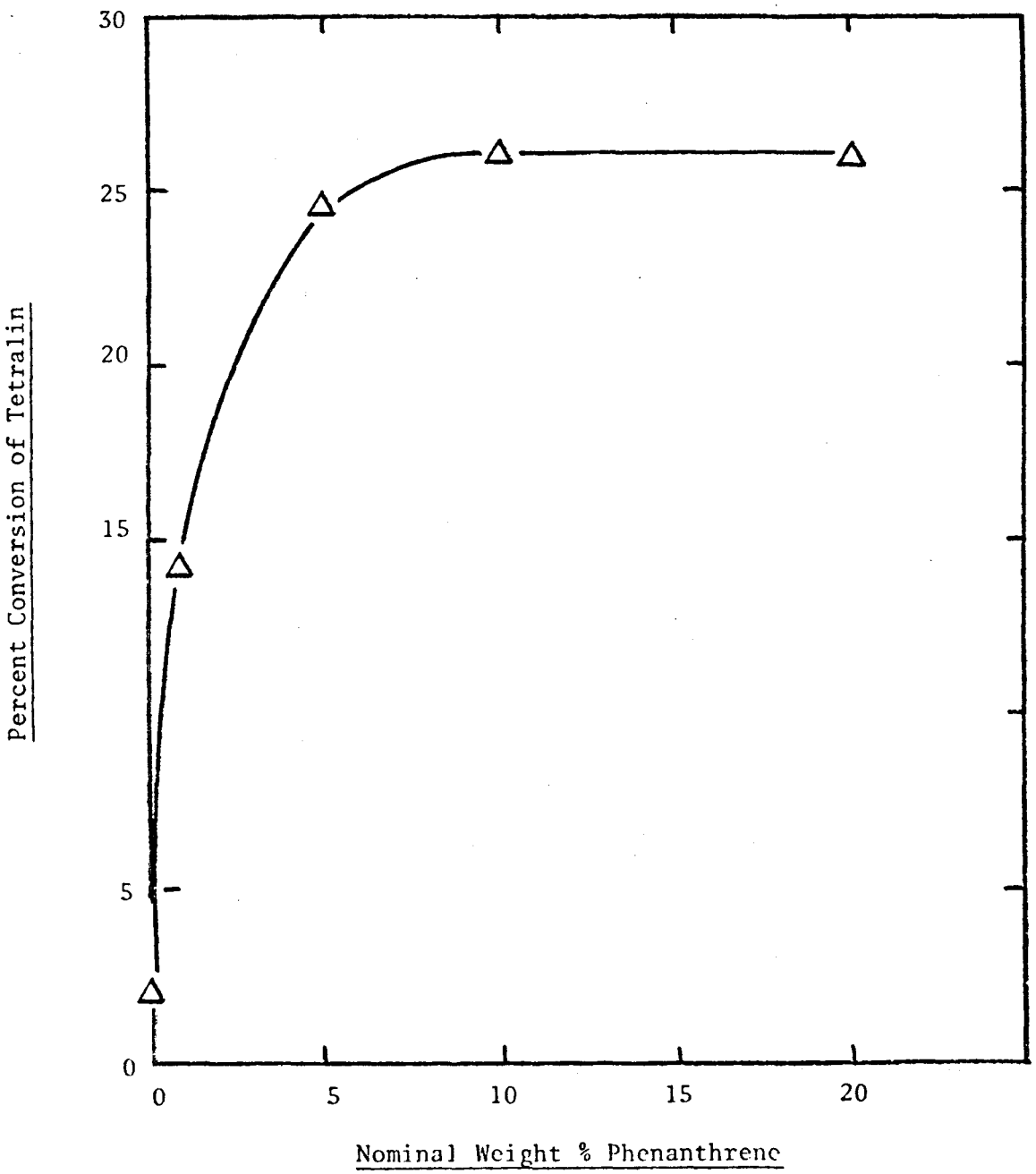


Table I

Tetralin/Phenanthrene Hydrogen Transfer Series

Run No.	Temperature °C	Feed Rate, cc/hr	Feed Composition, wt.%		Product Composition, wt.%		Conversion of Tetralin, %	Conversion of Phenanthrene, %	Nominal hold time, minutes
			Tetralin	Phenanthrene	Tetralin	Phenanthrenes			
917-3	425	9.93	96.91	-----	96.45	-----	0.47	-----	106
917-1	450	10.27	96.91	-----	96.28	-----	0.65	-----	103
917-2	475	10.03	96.91	-----	94.71	-----	2.27	-----	105
917-4	475	19.58	96.91	-----	94.64	-----	2.34	-----	54
918-3	425	10.25	78.25	18.86	75.52	16.96	3.49	10.07	103
918-1	450	10.42	78.25	18.86	73.21	17.33	6.44	8.11	101
918-2	475	10.17	78.25	18.86	60.23	16.50	23.03	12.51	104
918-4	475	20.03	78.25	18.86	66.34	16.82	15.22	10.82	53
919-1	475	10.32	96.78	-----	94.81	-----	2.04	-----	102
919-5	475	9.97	96.10	0.87	82.50	1.38	14.15	-----	106
919-3	475	10.28	92.27	4.50	69.65	3.66	24.50	18.67	103
919-4	475	10.09	87.13	9.46	64.51	7.66	25.96	19.03	105
919-2	475	10.41	78.54	18.34	58.18	16.03	25.92	12.60	101