Gas and Liquid Phase Pyrolysis of Tetralin- A Reconciliation of Apparently

Contradictory Data.

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ABSTRACT

The pyrolysis of tetralin under static reactor conditions at 450°C at

1-3 torr leads to hydrogen loss products (75%), C2 loss products (12%), and

neophyl radical rearrangement products (12%).   Tetramethylbutane initiated

the reaction and the product distribution was unchanged.   In the absence of

initiator the rate of reaction is near first order in tetralin.   The rate

is approximately 1/2 order in tetramethybutane.   A mechanistic scheme is

proposed which involves relatively fast hydrogen atom loss from the 1- or 2-

tetralyl radical followed by slow hydrogen atom abstraction or hydrogen atom

addition to tetralin, and formation of ring contracted product by reversible

neophyl rearrangement of the 2-tetralyl radical followed by rate determining

(in that pathway) hydrogen abstraction from tetralin.   In the absence of

external initiator, initiation by tetralin and termination by hydrogen atom

recombination dependent on total pressure, rationalizes the first order

behavior.   Liquid phase pyrolysis of tetralin at much higher concentrations

(ca 20000x) occurs with a rate only three times faster and 1-methylindan is

the major product.   The liquid phase reaction could be initiated with

tetramethylbutane and bibenzyl.   The change in product distribution and

rate between the more concentrated liquid phase pyrolysis and the dilute gas

phase pyrolysis can be rationalized by rate determining neophyl

rearrangement in the liquid phase because of fast hydrogen atom transfer

from tetralin to the resulting 1-methylindanyl radical.

END of ABSTRACT

Three major reaction paths have been identified[1] in the pyrolysis of tetralin: neophyl rearrangement to 1-methylindan in the liquid phase[2,3] retro Diels Alder reaction to benzocyclobutene and ethylene at low pressures under pulsed laser pyrolysis conditions[4] and in shock tube experiments[5]; and dehydrogenation under gas phase[6] and flash vacuum pyrolysis conditions.[8] Mechanistic questions concern the nature of the latter reaction and its relationship to the radical chain process for the neophyl rearrangement which occurs in the formation of 1-methylindan.[2,3] Bergman and Moore suggest that dehydrogenation is a heterogeneous process,[4] as do a number of previous investigators,[6] but Tsang has shown that addition of tetramethylbutane to tetralin gives dehydrogenation products under shock tube conditions at ca 1000°.[5] In the absence of this radical initiator and in the presence of excess methane, tetralin undergoes the retro Diels Alder reaction at higher temperatures in the shock tube with log k (/sec) = 15.54-79486/2.3RT. Also formed is o-allyltoluene with log k (/sec)=15.08-79700/2.3RT. o-Allyltoluene was also found to be a product in the laser pyrolysis experiments.   Trahanovsky and Yeung[9] have found that CW laser pyrolysis of tetralin at low pressures gives dehydrogenation products and argue that the pyrolysis temperature of the Bergman experiment is much higher than reported and is higher than in their experiment. The current project started as an attempt to find the initiator(s) responsible for the rearrangement of tetralin, but as recent experiments in other laboratories became known it was clear that a unifying mechanistic hypothesis is required

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and experiments were directed toward that end. Further, the various experiments described above were conducted under relatively exotic conditions so it appeared appropriate to attempt to reconcile the different observations by examining the system in a static well-conditioned gas phase reactor where heterogeneous effects have been minimized by treatment with dichlorodimethylsilane.

RESULTS

Under static reactor conditions at 450° and low pressures (1-3 torr) well-purified tetralin, tetH, undergoes hydrogen loss (ca 75% of the product) and rearrangement (ca 10%) and formation of styrene, sty, and ethylbenzene, etb, (ca 12%) and formation of 3-methylindene, 3mide, and 1-methylindan, 1mid, (ca 5%), and formation of indene, ide, and 2-methylindan, 2mid, and 2-methylindene, 2mide, (ca 7%)-see Table I. The extent of reaction is relatively independent of pressure of tetralin (with 7.2, 10.2, and 16.0 mg of tetralin in a 2l bulb, 91.7, 92.6, and 88.6 % of tetralin was recovered, respectively, after 11.5 hours). This suggests first order dependence on tetralin although there might be a slight concentration dependence which favors more ring contracted product. Nearly the same product distribution is obtained at shorter reaction times upon addition (1-3%) of the radical initiator, tetramethylbutane, tmb - see Tables I & II. The extent of reaction is dependent on the concentration of initiator to roughly the 0.5 power at roughly constant tetralin concentration. The structural changes are summarized in Scheme 1.

Scheme 1 here

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1-Methylindan is a likely precursor to indene and indenyl products as suggested by Franz and Camaioni,[3] and, indeed, pyrolysis of 1-methylindan under the same experimental conditions as described above gave indene, 3-methylindene, and 2-methylindene-see Table III. It is likely that 2-methylindene also results from dehydrogenation of 2-methylindan.

Since added initiator increases the rate of reaction without much changing the product distribution within each family (i.e. dehydrogenation, cleavage, and ring contraction), it must be concluded that the reaction is a radical chain process probably involving either the 1- or 2-tetralyl radical. Since the 2-tetralyl radical has been implicated as the intermediate in the liquid phase neophyl rearrangement of tetralin to 1-methylindan, it is tempting to suggest that all of the low temperature reactions are radical processes whose initiator has yet to be determined. The presence of excess methane in the shock tube experiments may quench radical processes involving tetralin to allow the retro Diels-Alder reaction to proceed. Just why the pulsed laser experiments proceed via a unimolecular process is not clear unless there was sufficient purification to remove an adventitious initiator or because the pressures might be much lower than those in the static and flash vacuum pyrolyses.

For completeness, liquid phase pyrolyses of neat tetralin were conducted. Thus, 30 microliter samples of tetralin were pyrolyzed at 450° in sealed tubes whose volume was estimated at 325-370 microliters. This corresponds to roughly 45 atmospheres of tetralin if all were in the vapor phase. Under these conditions the reaction was approximately three times faster than

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that in the gas phase at 1.2 torr. Further, 1-methylindan and naphthalene
are formed in a 3:1 ratio which is reversed from the dilute gas phase
reaction see Table IV. The loss of starting material correlates well with
an integrated first order rate equation, but correlation would be obtained
with all simple rate equations since the maximum percent conversion examined
was 15%. Added tetramethylbutane and bibenzyl promoted the reaction to the
same products but did so less efficiently than tetramethylbutane in the gas
phase-see Table V. Interestingly, at roughly 1/7th the concentration of
tetralin in the sealed tubes, the extent of conversion is the same, but the
ratio of 1-methylindane to naphthalene dropped to ca. 0.5.

DISCUSSION

Major questions in the static low and high concentration pyrolysis of
tetralin concern the mechanism of the reaction which must account for the
change in product distribution with concentration without a large change in
the overall rate of loss of starting material. Overall first-order
kinetics seem to be required, but there cannot be a three term rate
expression where dehydrogenation and cleavage are first order in tetralin
and the ring contraction reaction is second order at all concentrations so
that it is a minor pathway in the gas phase but dominates in the liquid
phase. Further, extrapolation of Tsang's shock tube kinetic data in the
absence of initiators to 450°C reveals that the unimolecular retro Diels-
Alder reaction and formation of allyltoluene occur much too slowly to be
considered as responsible for any product at this temperature. This

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observation and the response to radical chain initiators first observed by

Tsang strongly argue for a radical chain mechanism in the dilute gas phase

reaction.   The phenomenological rate expression which satisfies the

observed kinetics for the pyrolysis of tetralin is:

$$\text{Rate} = k_{obs}[\text{tetH}]^{1+x}[i_2]^{0.5}$$

where i_2 is an external initiator.

A mechanistic scheme which could rationalize the dehydrogenation kinetics

is one where the 1- or the 2-tetralyl radical undergoes scission of a beta

C-H bond to give a hydrogen atom and dihydronaphthalene (the major

dehydrogenation product at low conversions); also required is termination by

hydrogen atom recombination in order to obtain first order behavior in

tetralin.   This simple scheme therefore requires beta C-H bond fission to

occur faster than abstraction of hydrogen atom by hydrogen atom from

tetralin.   There may be concern that hydrogen atom recombination should

depend on the concentration of other materials in the system which would

introduce an inverse square root dependence of initiation on total

concentration.   The relative lack of dependence of the overall rate on

concentration would suggest that there is a square root dependence on

tetralin in the initiation to cancel the third body effect in the

termination.   In either event, Scheme 2 may be an appropriate descriptor of

the reaction.   Also included in Scheme 2 is a termination reaction

involving combination of hydrogen atom and the 2-tetralyl radical.   The

effect of this termination will be discussed much later, but the effect of

it will not dramatically alter the following discussion.   This scheme will

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also account for the formation of styrene since hydrogen atom can also add to tetralin at the ring fusion followed by two beta scission reactions liberating another hydrogen atom.[1] The scheme assumes that the hydrogen abstraction from and the hydrogen atom addition to tetralin are irreversible reactions, which is reasonable at low concentrations of dihydrogen, but at higher concentrations, the reversal is a reasonable pathway for recycling tetralin by hydrogenation. The formation of ring contracted products most likely occurs from a neophyl rearrangement of the 2-tetralyl radical to the 1-indanylmethyl radical followed by hydrogen atom abstraction from tetralin.[2] The indanylmethyl radical is less stable than the 2-tetralyl radical by 6 kcal/mole at room temperature[3] so that at low concentrations of tetralin, the 1-indanylmethyl radical probably reverts to the 2-tetralyl radical faster than it abstracts hydrogen from tetralin. This proposal recognizes that at higher concentrations of tetralin, the neophyl rearrangement may be rate determining since hydrogen abstraction may be fast compared with reversion of the 1-indanylmethyl radical to the 2-tetralyl radical. This can rationalize the increase in ring contracted product in the liquid phase reaction which occurs with only small increase in rate despite an enormous change in concentration of tetralin.

Scheme 2 assumes that only the 2-tetralyl radical (2-tet.) is important in forming observable products. No doubt the 1-tetralyl radical is formed often and allows hydrogen atoms to shuttle around, but it may be the less reactive species vis-a-vis the products obtained as has been demonstrated for formation of 1-methylindan in the liquid phase. Indeed, Poutsma[1] has

emphasized this conclusion based on thermochemical kinetic data provided by Franz and Camaioni.[3]

Using the steady state approximation with the long chain assumption, Scheme 2 provides the mechanistic rate equation, eq.1, for the dehydrogenation, cleavage, and ring contraction products where k_{obs} is the sum of the rate constants for abstraction of hydrogen atom from tetralin by hydrogen atom and addition of hydrogen atom to tetralin, and a ratio of rate constants whose value depends on the concentration of tetralin. This latter ratio also controls the ratio of ring contraction to other products in the reaction as a function of tetralin concentration.

eq. 1:

$$v = (k_{ad} + k_{ab} + k_{ab}*k_n*k_H*tetH/(k_1*(k_{-n}+k_H*tetH)))* \ tetH * (k_i*i_2/k_t*M)^{.5}$$

At low concentrations of tetralin, the equation reduces to eq. 2:

eq.2:

$$v = (k_{ad} + k_{ab} + k_{ab}*k_n*k_H*tetH/(k_1*k_{-n}))* \ tetH * (k_i*i_2/k_t[M])^{.5}$$

which indicates a second order dependence on tetralin concentration for the formation of the ring contracted product, but first order for all other processes, namely, dehydrogenation and cleavage which are the major pathways. At high concentrations of tetralin the equation reduces to eq. 3:

eq.3:

$$v = (k_{ad} + k_{ab} + k_{ab}*k_n/k_1)* \ tetH * (k_i*i_2/k_t)^{.5}$$

where all propagation processes have the same, first order, dependence on tetralin. The rate constant ratio of the third term of the rate equation 1 determines the rate difference at high and low concentrations of

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tetralin. At low pressures this ratio must be small compared with unity so the relative rate is $k_{ad} + k_{ab}$ plus some small fraction, but at higher concentrations of tetralin, the relative rate is $k_{ad} + k_{ab}$ plus a ratio which apparently is about three fold larger (i.e. k_n/k_1 is ca. three times k_{ab}). At low pressures, the rate ratio k_n*k_HtetH$/k_1*k_{-n}$ must therefore be about 1/40 of k_{ab} in the concentration range examined so the overall rate is not affected by tetralin concentration and yet this pathway is responsible for about 12% of the product. However, the relative amount of ring contracted products should have increased more increasing tetralin concentration in the gas phase experiments than was observed. Whether this discrepancy represents experimental error or an incomplete mechanistic scheme has yet to be determined, but the scheme does seem to account for most of the observations and is not inconsistent with the energy demands of each step.

The question of initiators in the dilute gas phase pyrolysis of purified tetralin is not resolved. Clearly, tetramethylbutane is an initiator of the same reactions so a radical initiation process must occur. As suggested above, if hydrogen atom recombination is responsible for termination (requiring a third body) then there must be a square root dependence on tetralin for initiation, a not unexpected possibility. Still another possibility for termination is hydrogen atom-tetralyl radical combination. If this is the sole termination reaction, the rate of the reaction is given by

$v = (k_{ad} + k_{ab})*$tetH$*k_1*i_2/k_t,*$tet. $+ k_n*k_H*$tetH$/(k_1*(k_{-n}+k_H*$tetH$))*$tet.

where the concentration of tet. is inversely proportional to hydrogen atom

concentration via the steady state relationship: tet. $= k_I * i_2 / k_t, * H$.
It would appear that tet. concentration would increase with increasing
tetralin concentration. If i_2 is tetralin (assuming unimolecular loss of
some impurity in tetralin or tetralin itself), the dehydrogenation and
cleavage reactions would be first order at all concentrations. However, the
ring contraction would be second order at low concentrations but first order
at high concentrations due to the change in rate determining step. All of
this is not inconsistent with the observations.

Among the extensive studies of this reaction is the report that
increasing concentrations of dihydrogen increases the extent of formation of
n-butylbenzene, and generally at the expense of formation of
naphthalene.[6c,7] This again suggests reversibility in the hydrogen atom
abstraction from tetralin.

There may be concern that hydrogen atom not only is responsible for the
chain but is the major odd electron species present in the reaction to
undergo termination.   The concern must focus on the relative rates of
unimolecular hydrogen atom loss from 2- (or 1-)tetralyl radical vs.
bimolecular hydrogen abstraction from tetralin by hydrogen atoms.   Poutsma
has calculated that these relative rates favor the bimolecular abstraction,
but only by a factor of less than six in the solution reaction and may favor
the unimolecular reaction in the gas phase.[1]   Further, the calculation is
based on a rate constant for beta hydrogen loss in 1,2-diphenylethyl radical
that has a preexponential term of only $10^{13.6}$/sec, a value which seems too
low by a factor of 10 to 100 when considering the 2- (or 1-) tetralyl
radical where the entropy price for olefin formation should be substantially

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less.   If indeed the preexponential term for hydrogen atom loss is in the range of 10^{14}-10^{15}/sec, then at higher temperatures, there should be more dehydrogenation, an observation made by Trahanovsky in an FVP experiment. Interestingly though, some benzocyclobutene is formed in the FVP experiment suggesting the onset of the unimolecular retro-Diels Alder reaction, which is the major reaction pathway in the shock tube experiments conducted at still higher temperatures due to the larger preexponential term as measured by Tsang.   This suggests that the Bergman-Moore laser-powered SiF_4 sensitized pyrolysis of tetralin at low pressures also occurred at a higher temperature than was estimated.   The hydrogen chain mechanism proposed with unimolecular initiation and third body dependent hydrogen plus hydrogen termination therefore appears consistent with most of the observations for the gas phase pyrolyses without recourse to heterogeneous effects like surface catalysis, and the change in mechanism is the result of the more entropically favored process at higher temperatures.

The diminished response to external initiators in the liquid phase experiments is not rationalized by the mechanistic scheme above although it might be suggested that bimolecular initiation using dihydronaphthalene, a small impurity in tetralin may be responsible.   In the experiments reported here, the tetralin was purified by washing with sulfuric acid then it was distilled from sodium. The amount of dihydronaphthalene present is less than 0.1% by gc.   Nonetheless, if the literature value for the molecule induced homolysis of dhn is used (log k(1/mole-sec)=10-36000/2.3RT; note that the preexponential term is impossibly high), the rate of initiation at 450° is roughly 10^{-7} mole/l-sec.   With 1% tmb initiator present, the rate

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of its decomposition is roughly 2×10^{-7} mole/l-sec assuming log k(/sec)=16.5-69000/2.3RT.[5]   Thus given some leeway dhn might be the dominant initiator in the high concentration regime at initial time, and this might provide the some increase in rate in the liquid phase reactions.   In addition, the major product is a ring contraction product resulting from, as suggested above, fast trapping of the 1-indanylmethyl radical making the faster reaction, the neophyl rearrangement of 2-tetralyl radical, the rate determining step of the propagation reactions.

Acknowledgment.

Experimental

^{1}H NMR spectra were recorded on a Nicolet model NT-360 (360 MHz) spectrometer. All chemical shifts were reported as parts per million (δ scale) from tetramethylsilane (TMS) and were taken in $CDCl_3$ solution. Mass spectra (MS) were obtained on a Kratos MS-80 spectrometer.

Gas chromatographic (GC) analyses were performed on a Varian 3700 gas chromatograph equipped with flame-ionization detector. Products were separated with a 50-meter DB-5 capillary column. Preparative GC was performed on a Varian-Aerograph Series Model 90-P using 12 ft. (12' x 1/4") 20% OV-101 column on chromosorb P.

Tetralin was obtained from Aldrich and was purified by standard procedures which includes washing with concentrated sulfuric acid until the washings are colorless and distillation from sodium.[10]   Tetralin obtained after purification was 99.9% pure by analytical GC containing naphthalene as impurity and was stored under Argon. Sample of 99.96% purity can be obtained by preparative GC. 1-Methylindan was obtained commercially and was purified by preparative GC.

Gas phase pyrolysis

Samples were pyrolyzed in a 300 ml and/or in a 2000 ml pyrex bulb submerged in a molten salt-bath composed of a 10:7 mixture of KNO_3 and $NaNO_2$ respectively. The temperature of the bath was maintained by two heaters. A 400-W Vycor resistance heater attached to a variable transformer was used to supply the majority of heat. A 250-W knife blade immersion resistance heater attached to an electronic temperature controller accurate to ±0.10°C was used for fine temperature control. Bath temperature was measured with a

calibrated platinum resistance thermometer with a precision of ±0.1°C. For the most purpose, the temperature of the bath was maintained at 450.6±0.1°C. The reaction bulbs were preconditioned at the pyrolysis temperature with dimethyldichlorosilane. Further conditioning was done with the respective samples used for pyrolysis. The pyrolysis bulbs were connected to a vacuum line which is capable of maintaining pressure at 10^{-3} torr. A cold finger was also attached to the vacuum line for easy transfer of high boiling materials into the reaction flask.

General Procedure: A definite amount of sample taken in a cold finger was thoroughly degassed. Using a hot water bath, a large portion of the sample was vacuum transferred from the cold finger into a reaction bulb. The rest of the sample was condensed back to the cold finger and was diluted with cyclohexane, and a standard was added. The solution was analyzed by capillary GC (using predetermined response factor) for left over starting material. From the difference, the amount of material pyrolyzed was determined. After pyrolyzing for a definite period of time, the pyrolysate was collected under vacuum to a coil trap cooled to liquid nitrogen. The pyrolysate was then collected back to the cold finger, diluted with cyclohexane and a standard was added. The thoroughly mixed solution was analyzed by capillary GC for products and unreacted starting material. Components were identified by comparison of ^{1}H NMR spectra, GCMS, and GC retention time with those of authentic materials.

Tetralin: Neat sample of tetralin of varying amounts was pyrolyzed in a bulb at 450.6°C for a definite period of time. The components of the

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pyrolysate were analyzed by GC using n-decane as a standard. The products were reported as mole percent based on reacted tetralin and were included in Table I. For products identification, tetralin was pyrolyzed for a longer reaction time. The pyrolysate was diluted with $CDCl_3$ and ^1H NMR was taken. Ethylbenzene, styrene, indan, indene, 1,2-dihydronaphthalene and naphthalene were identified in the ^1H NMR spectrum of the pyrolysate. This identification was substantiated by comparing GC retention time and GCMS data with those of authentic samples. Rest of the products were characterized by GC retention time and GCMS data. Authentic samples of 3- and 2-methylindene were obtained in the pyrolysis of 1-methylindan. These two compounds were isolated together by preparative GC and were identified by ^1H NMR spectra including proton decoupling experiments. Authentic sample of 2-methylindan was obtained in the pyrolysis of o-allyltoluene.

Tetralin and initiator 2,2,3,3-tetramethylbutane: A mixture of tetralin and initiator of different concentrations (weight percent) was pyrolyzed at 450.6°C for a definite period of time. The products identified were the same as in the absence of initiator. The results were reported in Table I and II.

1-Methylindan Pyrolysis

1-Methylindan was pyrolyzed in a static reactor with and without tetramethylbutane at 450.6°. The pyrolysate was analyzed by GC using n-decane as an internal standard. The product distribution are reported in Table III as mole percentages based on reacted starting material.

Liquid phase pyrolysis

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<u>General</u>: Samples were pyrolyzed neat in thick-walled pyrex ampules of 0.3-0.4 ml (total volume after sealing) which were degassed and sealed under vacuum. Tubes were suspended in the same $KNO_3:NaNO_2$ eutectic salt bath used for gas phase pyrolysis. The temperature was maintained at 450.4±0.2°C. Sealed sample tubes were preheated over a Bunsen Burner to attain a temperature of 220°-230°C before inserting into the salt-bath. This, thus, eliminated thermal shock and subsequent fracturing of tubes.

Samples were analyzed as dilute solutions in cyclohexane, 10-20 μl of pyrolysate in 1.0-1.5 ml of solvent with decane as internal standard. Appropriate response factors were used for estimating amounts of respective components.

<u>Tetralin</u>: Tetralin (neat) samples of ca. 30μl in ca. 350 μl tubes were pyrolyzed for different periods of time with and without tetramethylbutane or bibenzyl. The results appear in Tables IV and V. Four pyrolyses of 3-5μl in the 350μl tubes for 7324-7732 sec resulted in an average of 5% conversion to a 2:1 ratio of naphthalene to 1-methylindan.

<u>Synthesis of o-allyltoluene</u>. This compound was prepared by the method of Hurd and Bollman[11] and was purified by preparative GC. ^{1}H NMR 2.46 (s, 3 H), 3.48 (doublet of triplets, 2 H, J_d - 6.12 Hz, J_t - 1.44 Hz), 5.09 (app. doublet of quartets, 1 H, J_d - 16.92 Hz, J_q - 1.90 Hz), 5.17 (app. doublet of quartets, 1 H, J_{cis} - 10.44 Hz, J - 1.44 Hz), 6.06 (app. quartet of triplets (observed 10 lines), 1 H, J_{cis} - 10.44 Hz, J_{trans} - 16.92 Hz, J - 6.12 Hz), 7.24-7.40 (m, 4 H).

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Table I. Gas phase pyrolysis of tetralin and initiator.

Temperature = 450.6°±0.1°C
Volume of flask = 2 liter
Initiator = 2,2,3,3-tetramethylbutane (tmb)
Time = 41400 sec

	Tetralin Only			Tetralin + tmb (1%)		Tetralin + tmb (3%)		
Initial amount (mg) of (torr) tetH	7.16 mg ~1.22	10.21 mg 1.74	15.96 mg ~2.73	6.48 mg ~1.1	11.33 mg ~1.94	5.14 mg ~0.88	11.06 mg ~1.89	12.89 mg ~2.21
% Recovered tetH	91.70	92.60	88.62	77.33	60.28	51.61	49.29	38.90
Et-Ph	3.16	2.30	3.88	3.49	6.27	6.02	8.15	9.34
styrene	11.22	10.94	10.34	10.38	7.44	7.89	6.19	4.95
indan	---	---	0.66	---	0.64	0.47	0.69	0.95
indene	4.11	3.91	3.91	4.60	5.19	5.63	5.61	5.94
2-me-indan	---	---	0.59	0.52	0.52	0.58	0.53	0.46
1-me-indan	1.24	2.16	1.78	1.06	1.60	1.17	1.71	1.73
3-me-indene	3.58	4.46	3.49	3.45	3.48	3.75	3.45	3.42
2-me-indene	2.48	2.70	2.44	3.03	3.11	3.55	3.19	3.24
dhn	60.20	60.94	53.90	53.49	42.13	36.32	33.17	25.40
nap	13.96	12.84	18.99	19.90	29.62	34.56	37.29	44.57

Table II. Gas phase pyrolysis of tetralin and initiator.

Temperature = 450.6±0.1°C
Volume of flask = 2 liter
Substrate = Tetralin (tetH)
Initiator = tmb
Time = 7200 sec

	Initiator 2.12%		Initiator 2.83%		Initiator 6.1%	
initial amount of tetH (mg)	-4.75	4.31	4.11	4.20	4.74	
Recovered tetH (%)	88.0	83.92	85.95	78.62	76.46	
Et-Ph	2.34	2.56	2.41	4.37	3.74	
styrene	12.03	11.70	12.05	10.94	10.63	
indene	3.12	3.37	3.15	3.52	3.52	
2-me-indan	0.45	0.45	0.85	---	0.67	
1-me-indan	0.83	0.99	1.04	0.80	1.09	
3-me-indene	4.69	4.66	4.57	4.39	4.46	
2-me-indene	1.57	1.58	1.53	1.45	1.53	
dhn	61.30	62.89	61.67	59.84	56.45	
nap	13.64	11.75	12.71	14.67	17.88	

Table III. Gas phase pyrolysis of 1-methylindan and initiator (tmb) at 450.6±0.1°C.

	1-methylindan only		1-me-indan + tmb (2-3%)	
Initial amount (mg) of 1-me-indan	2.64	2.71	17.28	2.75
Recovered 1-me-indan (%)	51.84	94.54	59.0	62.98
Me-Ph	*	3.82	5.17	5.23
Et-Ph	3.26	4.08	4.34	2.83
Styrene	0.89	5.07	1.03	2.73
indan	3.83	1.91	2.60	1.02
indene	25.91	11.87	19.66	20.47
2-me-indan	3.67	3.94	4.17	3.32
3-me-indene	30.26	46.05	34.02	32.50
2-me-indene	22.14	10.53	21.12	21.07
tetralin	4.36	8.45	3.35	4.22
dhn	1.83	4.16	1.39	2.56
nap	3.77	--	3.12	3.98
time (sec)	79200	7200	41400	41400
Vol. of flask (ml)	300	2000	2000	2000

* not determined ≈ 2-3%

Table IV. Pyrolysis of tetralin in sealed tubes.

Temperature - 450.4°C
30 μl sample of tetH
Volume of sealed tube - 325 - 370 μl
Molarity - 0.65 - 0.74 M

Recovered tetH (%)	96.64	95.66	93.16	92.77	90.95	87.10
1-me-indan	2.48	3.46	4.56	5.56	7.44	9.65
nap	0.88	0.87	2.28	1.68	1.60	3.23
time(sec)	5350.	7322.	7258.	11433.	14580.	18808.

* Minor products: indene and 2-methylindan.

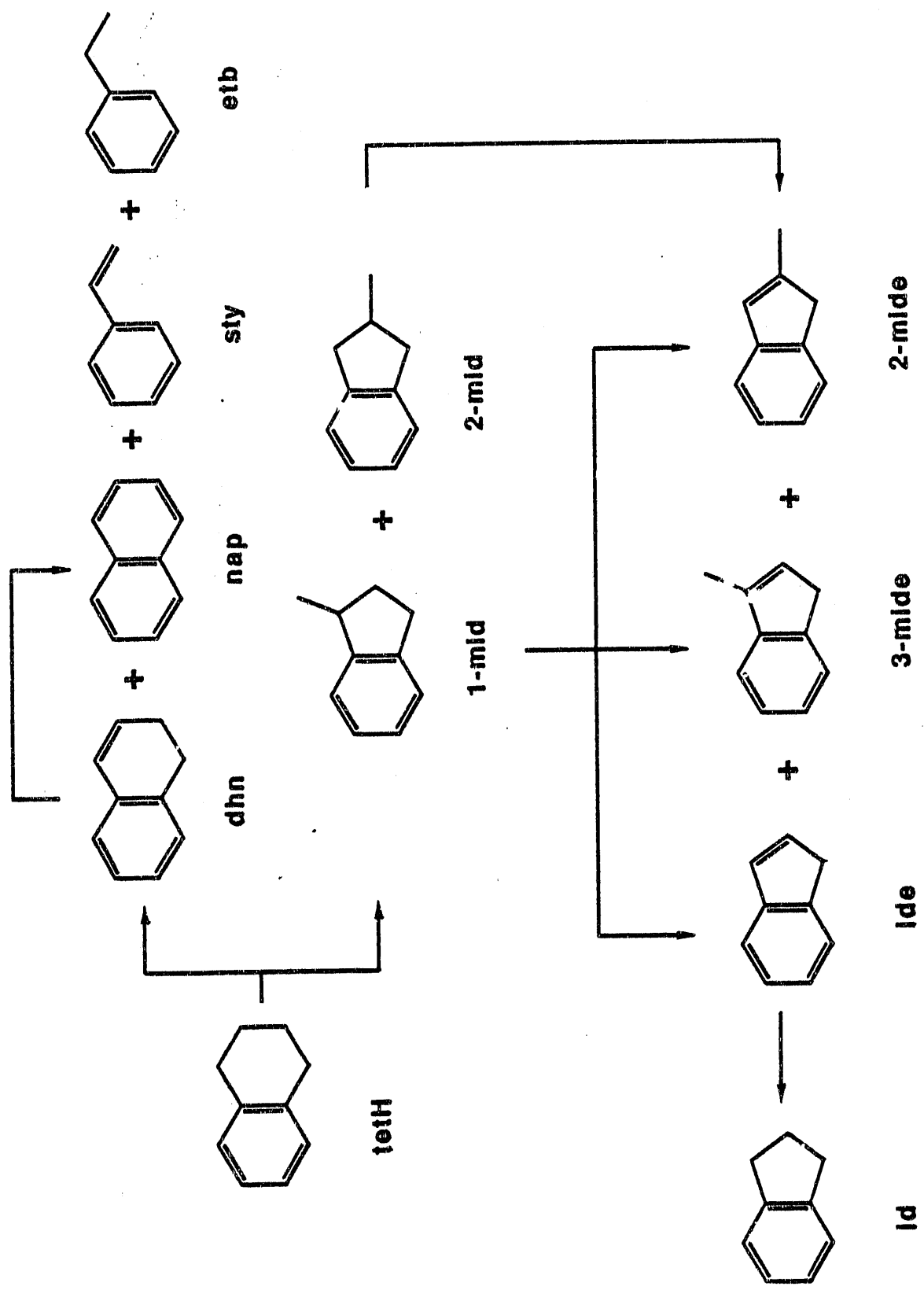
Table V. Pyrolysis of tetralin and initiators in sealed tubes at 450.2°.

Temperature - 450.2°C
30 μl sample of tetH
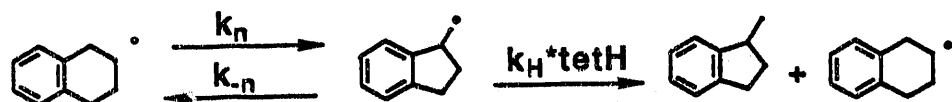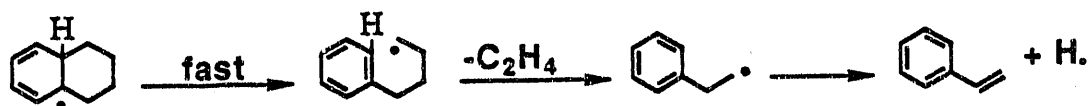Volume of sealed tube - 325 - 370 μl
Molarity - 0.65 - 0.74 M

	tetH only	tetH + 7.5% tmb	tetH + 11.9% tmb	tetH + 15.3% tmb	tetH + 5.8% Bz$_2$
Recovered tetH (%)	93.47	83.86	80.59	78.37	81.42
indene	0.29	0.77	1.00	1.11	0.82
2-me-indan	0.19	0.41	0.39	0.50	0.50
1-me-indan	4.10	9.06	10.58	11.24	10.68
nap	2.43	5.89	7.44	8.78	6.58
time(sec)	7198.	7220.	7396.	7236.	7460.

Bz$_2$ - bibenzyl

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Scheme 1

etb

sty

nap

dhn

tetH

2-mId

1-mId

2-mIde

3-mIde

Ide

Id

Scheme 2

$i_2 \xrightarrow{k_I} 2\,I\cdot \xrightarrow{k_{iI}\,*}$ [tetralin] $\quad iH +$ [tetralinyl radical]

[2-tetralyl radical] $\xrightarrow{k_1}$ [dihydronaphthalene] $+ H\cdot$

2-tet.

$H\cdot +$ [tetralin] $\xrightarrow{k_{ab}}$ $H_2 +$ [tetralinyl radical] [reversible at high H_2 concentrations]

$H\cdot +$ [tetralin] $\xrightarrow{k_{ad}}$ [H-adduct radical]

[H-adduct radical] $\xrightarrow{\text{fast}}$ [radical] $\xrightarrow{-C_2H_4}$ [benzyl-type radical] $\longrightarrow$ [styrene] $+ H\cdot$

[tetralinyl radical] $\underset{k_{-n}}{\overset{k_n}{\rightleftarrows}}$ [indanyl radical] $\xrightarrow{k_H * tetH}$ [methylindan] $+$ [tetralinyl radical]

[k_H rate determining at low tetH, k_n rate determining at high tetH]

$2\,H\cdot\;[+M] \xrightarrow{k_t} H_2\;[+M] \qquad (H\cdot + 2\text{-tet.} \xrightarrow{k_{t'}} tetH)$

$$\text{Rate} = \left(k_{ad} + k_{ab} + k_{ab} \left(\frac{k_n * k_H * tetH}{k_1 * (k_{-n} + k_H * tetH)} \right) \right) * tetH * \sqrt{\frac{k_I * i_2}{k_t M}}$$

END

DATE
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10 / 27 / 92