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FLOW PYROLYSIS AND DIRECT AND SiF_4 -SENSITIZED LASER-INDUCED
DECOMPOSITION OF TETRALIN. IDENTIFICATION OF RETRO-[2+4]
CLEAVAGE AS THE PRIMARY HOMOGENEOUS THERMAL DECOMPOSITION CHANNEL

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Flow Pyrolysis and Direct and SiF_4 -Sensitized Laser-Induced
Decomposition of Tetralin. Identification of Retro-[2+4]
Cleavage as the Primary Homogeneous Thermal Decomposition Channel

By Michael R. Berman, Paul B. Comita,
C. Bradley Moore and Robert G. Bergman

Abstract

In an effort to determine the products and mechanism of the truly homogeneous thermal decomposition of the aromatic hydrocarbon tetralin, we have examined the products formed from this compound upon energization by conventional flow pyrolysis, infrared multiphoton excitation, and SiF_4 -sensitized infrared laser thermal activation. Six major products are formed in these reactions, but the product ratios depend upon the mode of energization. Flow pyrolysis gives a result analogous to those observed earlier; i.e., almost exclusive dehydrogenation, leading to dihydronaphthalene and naphthalene. Direct and sensitized IR laser-induced decomposition, however, leads to ethylene loss (presumably by an initial retro-[2+4] reaction) as the predominant decomposition mode, giving benzocyclobutene. We believe these results are due to the fact that direct thermal decomposition, both in our experiments as well as in previous studies, involves predominant surface-catalysis. In the laser-induced reactions, which are uncomplicated by problems due to surface-catalysis, the true homogeneous decomposition takes place, and this involves retro-[2+4] cleavage. Mechanistic details of these processes were studied by examining the isotope distribution in the products formed on SiF_4 -sensitized laser photolysis of 1,1,4,4-tetradeuteriotetralin.

Flow Pyrolysis and Direct and SiF_4 -Sensitized
Laser-Induced Decomposition of Tetralin.
Identification of Retro-[2+4] Cleavage as
the Primary Homogeneous Thermal Decomposition Channel.

Sir:

The thermal chemistry of tetralin (1) has been under intense investigation recently¹, due to interest in the fate of hydrogen donors which are used as recycle liquids in the solvent refining of coal. The reactivity of tetralin appears to be dependent on the presence of hydrogen, hydrogen acceptor molecules, different types of reactor surfaces, and surface history. This has resulted in conflicting data² in the literature and confusion as to what the thermal reactivity is in the absence of any catalytic effects. In an effort to resolve this situation, we wish to report the reactivity of tetralin resulting from several different methods of activation.

Three methods for energization of 1 were investigated: conventional flow pyrolysis, infrared multiphoton excitation, and sensitized infrared laser thermal activation. All three give rise to six major products: benzocyclobutene (2), styrene (3), o-allyltoluene (4), indene (5), 1,2-dihydronaphthalene (6), and naphthalene (7) (see Scheme 1), and several minor products³. The primary concern of this work is to delineate the energetics of the ethylene-loss channel (giving rise to 2 and 3) versus the hydrogen-loss channel (giving rise to 6 and 7) without

interference from catalytic effects.

A number of parameters affected the product distribution for the decomposition in a flow reactor⁴, including the composition of the surface, the history of the surface, and the pressure of the system (see Table 1). However, dehydrogenation was always the predominant decomposition mode. Unconditioned surfaces, higher pressures, and longer contact times in the reactor led to more dehydrogenation of 1.

Multiphoton excitation of 1 in the gas phase was accomplished⁵ with a pulsed CO₂ TEA laser^{6,7} tuned to 945.99 cm⁻¹. All six major products⁸ found from the pyrolysis also resulted from photolysis of tetralin, including one additional product, phenylacetylene⁹. The distribution of these products, however, was at variance with the distribution from the pyrolysis (see Table 1); the major reaction channel for the multiphoton dissociation of tetralin involved ethylene loss.

In the third method of activation, 1 and varying pressures of SiF₄, an inert sensitizer¹⁰ which absorbs strongly in the infrared, were irradiated¹¹ with an unfocused, pulsed CO₂ TEA laser tuned to 1027.36 cm⁻¹. Pure tetralin does not decompose under unfocused conditions; thus all chemistry is due to sensitization by SiF₄. All six major products were again found.

The number of pulses and the maximum temperature¹² of SiF₄ both had pronounced effects on the product distribution. The variation in the number of pulses had a number of effects. With increasing number of pulses the percentage of 2 and 6 decreased, and the percentage of 3, 5, and 7 increased. This is

consistent with 2 and 6 being primary products, and at least some fraction of 3, 5, and 7 being derived from them. Sensitized photolysis¹³ of 2 gave rise to a clean isomerization to 3, the sole product of the reaction (70% conversion). Sensitized photolysis¹³ of 6 (20% conversion) gave rise to two major products¹⁴, 7 (68% of product) and 5 (11%).

Temperature variation was achieved by changing the beam intensity and by varying the sensitizer pressure. Less secondary decomposition took place at lower temperatures, and there was a partitioning between the retro-[2+4] channel and the dehydrogenation channel (see Table 1). The ethylene-loss channel increased relative to dehydrogenation as the temperature was lowered, consistent with it being the low energy reaction channel for tetralin.

In order to further elucidate the mechanism of reaction of tetralin, 1,1,4,4-tetradeuteriotetralin ($1-d_4$) was synthesized¹⁵ and subjected to sensitized photolysis. The labeling results¹⁶ indicate that the retro-[2+4] product results entirely from C_2H_4 loss and the dehydrogenation is predominantly a result of 1,2-elimination (see Table 2).

Since thermal 1,2-elimination of hydrogen is unusual¹⁷, the nature of this reaction is of interest. The surface to volume ratio¹⁸ for the photolysis cell had no effect on the ratio of ethylene-loss/dehydrogenation for the sensitized photolysis. The possibility of a radical chain mechanism for the dehydrogenation was tested for by charging the photolysis cell with 1 Torr of

nitric oxide. The only observed effect of nitric oxide was to lower the effective temperature for the photolysis. A decrease in the partial pressure of tetralin from 0.325 Torr to 0.032 Torr also had no effect on the ratio of ethylene-loss to dehydrogenation.

We draw the following conclusions from the above experiments: (1) Some fraction of the dehydrogenation reaction in the flow reactor is surface catalyzed. This leads to an anomalously large amount of 1,2-dihydronaphthalene and naphthalene in the reaction products in these flow pyrolysis studies and very likely in all previous investigations. (2) The lowest energy homogeneous reaction channel for tetralin is the retro-[2+4] channel giving rise to benzocyclobutene. This fact is borne out in both the multiphoton and SiF_4 sensitized experiments where surface chemistry does not appear to be important. (3) The low energy dehydrogenation channel of tetralin is almost exclusively 1,2-dehydrogenation. This process, if concerted, is symmetry forbidden and without precedent as the lowest energy dehydrogenation channel in cyclic olefins. Evidence for a radical pathway by radical scavenging experiments was not found. Bimolecular pathways for this process were also not detectable by changing the partial pressure of 1.

The reactivity of tetralin contrasts with that of its olefinic analog cyclohexene¹⁷ in a number of ways. The rate of the retro-[2+4] reaction is more nearly comparable to that of dehydrogenation in tetralin, resulting in competitive formation of 6 and 7 with 2 and 3. If the retro-[2+4] reaction in tetralin

is concerted, disruption of the aromatic nature of the ring system may give rise to a higher energy transition state for ethylene loss. If the concerted pathway is shunned due to this situation, a stepwise carbon-carbon bond cleavage with subsequent loss of ethylene may be occurring. In either case, one would expect a higher activation energy for the ethylene-loss channel, one more nearly comparable to that of dehydrogenation. The observation of o-allyltoluene, the disproportionation product from the intermediate in a stepwise process, indicates that the non-concerted reaction is energetically feasible. The occurrence of 1,2- instead of 1,4-dehydrogenation is perhaps not surprising since again the aromatic nature of the ring system must be destroyed for a concerted 1,4-hydrogen elimination to occur. Questions as to the energetics of these processes and their mechanisms are under active investigation.

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References and Notes

- (1) a) A. G. Loudon, A. Maccoll, and S. K. Wong, J. Chem. Soc. (B), 1733 (1970); b) R. J. Hooper, H. A. J. Battaerd and D. G. Evans, Fuel, 58, 132 (1979); c) P. Bredael and T. H. Vinh, Fuel, 58, 211 (1979); d) B. M. Benjamin, E. W. Hagaman, V. F. Raaen and C. J. Collins, Fuel, 58, 386 (1979); e) T. Gangwer, D. MacKenzie, and S. Casano, J. Phys. Chem., 83, 2013 (1979).
- (2) For example, compare references 1a and 1e for the static pyrolysis results.
- (3) The minor products have been tentatively identified as toluene, ethylbenzene, 1,4-dihydronaphthalene, and o-ethylstyrene. Traces of other unidentified aromatics were also observed. In nearly all experiments, none of the above products amounted to more than one percent of the total reaction mixture.
- (4) See M. D'Amore, R. G. Bergman, M. Kent and E. Hedaya, Chem. Comm., 49 (1972), for a description of the flow reactor.
- (5) A sample cell consisted of a 2 cm i.d. by 20 cm long pyrex cell with KCl windows mounted at the Brewster angle. The cell was pumped to $<10^{-5}$ Torr on a grease-free vacuum line and was pressured to 0.325 Torr of 1 for all photolysis experiments. Pressures of all gases were measured with a capacitance manometer.
- (6) The laser pulse consisted of a 100 ns pulse followed by a 1 ps tail with an approximately 50:50 energy distribution

- between the pulse and tail. The energy per pulse was 1.3 Joules.
- (7) A 15 cm focal length NaCl lens was used to focus the beam. During a photolysis, the focal point was located at approximately the midpoint of the cell. The laser beam was attenuated by placing a gas cell containing SF₆ in front of the photolysis cell. The intensity was varied by varying the pressure of SF₆. The energy density at the focal point was 46 Joules/cm² at 0.8 Joules/pulse and 23 Joules/cm² at 0.4 Joules/pulse.
  - (8) At low fluences 7 was not observed, presumably due to lack of secondary decomposition of 6.
  - (9) Phenylacetylene was identified by GC-MS of the photolysis mixture. It was not a product in the flow pyrolysis or sensitized photolysis. In the direct irradiation experiments, this product could result from dehydrogenation of vibrationally excited styrene.
  - (10) K. J. Olzyna, E. Grunwald, P. M. Keehn, and S. P. Anderson, Tet. Lett., 1609 (1977).
  - (11) The photolysis cell for the sensitized photolysis was 4.5 cm i.d. by 4 cm long. The energy/pulse ranged from 0.11 to 0.27 Joules/pulse and the beam diameter was 0.7 cm. The energy absorbed ranged from 0.024 to 0.14 Joules/pulse. The variation in beam intensity was achieved as described in reference 7.
  - (12) The initial temperature after a pulse was calculated assuming all absorbed energy is statistically distributed

among all of the degrees of freedom of SiF_4 and 1.

- (13) Photolysis condition¹⁰: 300 shots, 0.27 Joules/pulse, 5 Torr SiF_4 and 0.325 Torr 2 or 6.
- (14) Minor products were 1,4-dihydronaphthalene (7% of product), 1 (5%), 3 (3%), and six unidentified products (total 5.9%).
- (15) Tetralin labelled with deuteria in the benzylic positions was obtained by treating 1 with D_5 -dimesyl anion in D_6 -dimethylsulfoxide.
- (16) Analyses for isotope distribution in each of the pyrolysis products of 1- d_4 were obtained by GC-MS. The mass spectra were obtained at 15 eV.
- (17) D. C. Tardy, R. Ireton, and A. S. Gordon, J. Am. Chem. Soc., 101, 1508 (1979).
- (18) The surface to volume ratio was increased by a factor of four by using a cell 4.5 cm i.d. by 1 cm long.

Scheme 1

Table 1. Product distribution for thermal reaction of 1.

Conditions	Products (%)							% conversion of 1
	2	3	4	5	6	7	other	
Flow pyrolysis, 1 atm. N ₂ , quartz reactor, 750°C.	2.4 ^{a,b}	18.3	0.5	17.5	10.7	45.8	4.2	74.8
Vacuum flash pyrolysis, 0.05 Torr, quartz reactor, 750°C.	34.7	9.9	7.9	4.1	31.8	8.2	3.4	3.7
Multiphoton excitation, 0.325 Torr 1, energy/pulse 0.4 Joules, 13,020 pulses.	72.6	11.7 ^c	3.4	4.2	6.2	0.0	2.0	0.5
Multiphoton excitation, ^d 0.325 Torr 1, energy/pulse 0.8 Joules, 2790 pulses.	54.8	19.7 ^c	2.6	5.5	9.0	trace	8.4	0.8
SiF ₄ sensitization, ¹¹ T _{max} = 650°C, 5 Torr SiF ₄ , 0.325 Torr 1, 4960 pulses.	58.5	8.3	20.8	2.2	10.3	0.0	0.0	1.5
SiF ₄ sensitization, ¹¹ T _{max} = 1490°C, 6 Torr SiF ₄ , 0.325 Torr 1, 180 pulses.	38.2	20.1	8.4	9.4	15.5	5.6	2.8	7.7

^aNumbers are percent of total product found. ^bAll data have been corrected for FID response.

^cIncludes phenylacetylene response. ^dVisible emission in the focal region was observed in this experiment.

Table 2: Deuterium labeling in products from photolysis of 1-d_4^a .

Product	% of total mixture	Isotopomer (%)			
		d_4	d_3	d_2	d_1
2	57.8	100 ^{b,c}	0	0	0
3	10.6	32	8	29	31
4	8.2	100	0	0	0
5	4.2	0	42	43	15
6	12.8	10	83	7	0
7	2.3	0	1	95	4

^aPhotolysis conditions: 1-d_4 (0.325 Torr) was irradiated with 300 pulses, 0.27 Joules per pulse, with 5 Torr SiF_4 . T_{max} was 1430°C . ^bThe numbers are the percent of product with the indicated number of deuterium atoms as determined by GC-MS analysis. ^cThe data are corrected for ^{13}C natural abundance and 98.7% deuterium incorporation in 1-d_4 .