methanesulfonyl chloride-catalyst complex initially formed, with subsequent formation of SO_2 and other products.

The rate law reported herein, zero order in aromatic hydrocarbon concentration, appears to rule out this second proposed mechanism in that this S_N2-like mechanism predicts rate law dependence upon this concentration.

The first proposed mechanism involves loss of SO_2 before reaction of the evolved electrophile with aromatic hydrocarbon. We attempted to measure the rate of SO_2 evolution by following increases in gas volume as a function of time in a benzene run. The rate, $k_2 = 1.9 \times 10^{-2} \text{ M}^{-1}$ s⁻¹, is within experimental error of " k_{B} " (see Table I) measured noncompetitively. This supports the proposal that SO_2 is released during formation of the electrophile.

Although there is little evidence for ionization of sulfonyl chlorides,12 one study of the thermal decomposition of phenylmethanesulfonyl chloride has been interpreted in terms of benzyl cation formation.¹³ To explain the little variation in product isomer distribution with changes in catalyst, the benzyl cation has been suggested as the common electrophile in the benzylation of toluene using benzyl chloride in excess aromatic hydrocarbon.^{4b} It appears the same is valid for this reaction carried out in nitromethane, nitrobenzene, or sulfolane.¹¹ The results we obtained by using phenylmethanesulfonyl chloride are similar to those obtained using benzyl chloride.⁶ Furthermore, competitive results, see Table III, obtained using (p-chlorophenyl)methanesulfonyl chloride are similar to those obtained using *p*-chlorobenzyl chloride.¹⁴ We therefore conclude that there is a common electrophile for catalyzed benzylation carried out with either benzyl chlorides or phenylmethanesulfonyl chlorides and suggest that the common electrophile is the benzyl cation.

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Registry No. BSC, 1939-99-7; PCBSC, 6966-45-6; AlCl₃, 7446-70-0; benzene, 71-43-2; toluene, 108-88-3; o-benzyltoluene, 713-36-0; m-benzyltoluene, 620-47-3; p-benzyltoluene, 620-83-7; o-(p-chlorobenzyl)toluene, 55676-88-5; m-(p-chlorobenzyl)toluene, 91410-28-5; p-(p-chlorobenzyl)toluene, 30203-87-3.

Evidence for Concerted Transfer of Hydrogen from Tetralin to Coal Based on Kinetic Isotope Effects

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The H/D kinetic isotope effects for the reaction of subbituminous coal with tetralin- d_{12} , tetralin- $1,1,4,4-d_4$, and tetralin-2,2,3,3-d4 are respectively 3.7, 2.0, and 2.0. This pattern is consistent with concerted transfer of a pair of hydrogen atoms from the 1- and 2-positions. It does not result from exchange of hydrogen in unreacted tetralin and is difficult to explain as an anomalous secondary effect. The H/D kinetic isotope effects for 1,2-dihydronaphthalene- d_{10} and $-1,1,3-d_3$ are 2.7 and 1.1. The latter appears to be a typical secondary effect. The rate-determining step is thought to be transfer of a single hydrogen from the 2-position, probably as hydride ion. The activation volume for 1,2-dihydronaphthalene is -23 mL/mol. This result is consistent with the proposed mechanism or almost any other bimolecular mechanism.

In recent years much effort has gone into the study of the chemical details of the reaction of coal with hydrogen donor solvents such as 1,2,3,4-tetrahydronaphthalene (tetralin). Most investigators adopt the hypothesis of Curran, Struck, and Gorin¹ that the coal molecule homolyzes and the free radicals abstract hydrogen atoms from the donor as shown in Scheme I. Several studies²⁻⁸ have involved the use of model compounds of such constitution that they homolyze at reasonable rates at temperatures near 400 °C and conform to the types of structure which could occur in coal. A special type of model compound having a three-atom bridge between aromatic rings can react by a radical chain mechanism⁹⁻¹¹ with a faster rate than substrates which simply homolyze to benzylic or aryloxy radicals. It is uncertain how abundant such structures would be in coal. A problem with all of the free radical model compounds is that they are less reactive than

Scheme i

$$COAL \xrightarrow{slow} R' + R'$$

$$() + R' \longrightarrow () + RH \xrightarrow{repeated}_{loss of H} ()$$

coal even though ideal examples are chosen. Our sample of coal has the same half-life for conversion of tetralin to

- Chem. Fundam. 17, 291 (1979). (4) Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Modi, R. J. Ind. Eng.
- Chem. Fundam. 1979, 18, 153. (5) Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Modi, R. J.; Seshadri,
- (b) Cronater, D. C.; Jewen, D. M.; Snan, Y. T.; Modi, R. J.; Sesnadri,
 K. S. Ind. Eng. Chem. Fundam. 1979, 18, 368.
 (c) Hooper, R. J.; Battaerd, H. A. J.; Evans, D. G. Fuel 1979, 58, 132.
 (c) Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Maupin, P. H.; Roard,
 W. H. J. Am. Chem. Soc. 1979, 101, 5009.
 (8) Franz, J. A.; Camaioni, D. M. J. Org. Chem. 1980, 45, 5247.
 (9) Gilbert, K. E.; Gajewski, J. J. J. Org. Chem. 1982, 47, 4899.

⁽¹²⁾ Olah, G. A.; Ku, A. T.; Olah, J. A. J. Org. Chem. 1970, 35, 3925-3928. (13) Thoi, H. H.; Iino, M.; Matsuda, M. J. Org. Chem. 1980, 45, 3626-3630.

⁽¹⁴⁾ DeHaan, F. P.; Delker, G. L.; Ahn, J.; Chang, J.; Cowan, R. L.; Chicz, R. M.; Kim, J. Y.; Meinhold, R. W.; Roberts, M. P.; Stoler, E. M.; Tang, M.; Williams, E. L., manuscript in preparation.

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⁽¹⁾ Curran, G. P.; Struck, R. T.; Gorin, E. Ind. Eng. Chem. Process (1) Curling, Gr. 11, Gr. 11,

naphthalene at 335 °C which bibenzyl has at 405 °C. The thermolysis of 1.3-diphenylpropane¹⁰ has a comparable rate at 365 °C.

Other workers believe that the reaction proceeds partly if not mainly by other mechanisms. Ross¹² has proposed a hydride-transfer mechanism which is analogous to a number of reductive preparative procedures in organic chemistry such as borohydride reduction, the Leuckart reaction, the Meerwein-Ponndorf-Verley reduction, etc. Virk¹³ has proposed a pericyclic pathway and has reported some experiments to establish its feasibility for model compounds.¹⁴ The validity of these particular experiments involving the dihydronaphthalenes with phenanthrene and anthracene has become doubtful in the light of other investigations,^{15,16} but the pericyclic mechanism may yet apply to other types of reactant.

We have reported the effects of pressure and isotopic substitution on the rate of reaction of coal with tetralin.¹⁷ The molar activation volume measured at 344 °C was -27 \pm 3 mL which indicates a transition state characterized by increased bonding. There may also be a contribution due to ionic electrostriction. It is not compatible with a mechanism in which the rate is controlled by free radical generation. The H/D kinetic isotope effect for tetralin deuterated at the α -positions was 2.1 ± 1 at 335 °C: Almost simultaneously Cronauer¹⁸ reported measurements which give the same value when analyzed by the method described below. The existence of a kinetic isotope effect is incompatible with rate-controlling homolysis. It should be emphasized that the theoretical upper limit for a primary kinetic isotope effect at this temperature is 2.5. Both results are consistent with the hydride-transfer mechanism and the pericyclic mechanism or any other mechanism having a transition state which is not unimolecular and in which the C-H bond is partly broken.

A logical extension of the application of the kinetic isotope effect is to compare the effects of α -deuteration, β -deuteration, and perdeuteration in order to determine whether the loss of hydrogen atoms from the two positions is consecutive or concerted. If the loss of hydrogen atoms is stepwise and the rate is controlled by loss of the first hydrogen atom (presumably from an α -position) then α -deuterated and perdeuterated tetralin would give the same isotope effect except perhaps for a small secondary effect. With β -deuterated tetralin there should only be a secondary effect. If, on the other hand, the pericyclic mechanism obtains, the relative rates for undeuterated, α -deuterated, β -deuterated, and perdeuterated tetralin would have the proportions $1:X:X:X^2$, which is to say, 1:0.5:0.5:0.25. 1,2-Dihydronaphthalene, which is much more reactive than tetralin, can also be conveniently deuterated in the 1- and 3-positions and perdeuterated for a parallel series of measurements.

Results and Discussion

Tetralin. The course of formation of naphthalene in the reaction of tetralin and its deuterated derivatives with a subbituminous coal sample is shown in Figure 1. The



Figure 1. Reaction of coal with tetralin. Percent naphthalene vs. time in hours

Table I. Relative Reaction Times for Deuterated Tetralins

_				A DEC AN ADDRESS OF AD		
	% C ₁₀ H ₈	d_0	<i>d</i> ₁₂	1,1,4,4-d ₄	2,2,3,3-d4	
	9	(1.0)	3.5	1.75	1.70	
	12	(1.0)	3.2	1.71	1.71	
	15	(1.0)	3.0	1.75	1.74	
	18	(1.0)	3.1	1.76	1.75	

weight percentage of naphthalene in the C_{10} fraction of partially reacted mixtures is plotted against time in hours. The starting mixture contained equal weights of powdered coal and tetralin, and the temperature was 335 °C. The kinetic isotope effect can be extracted without the need of assuming any particular rate law provided the effect is independent of the degree of conversion. This proviso can be tested experimentally, and it is found to be satisfied. Smooth curves are drawn through the points, and the region from 9% to 18% naphthalene where the separations of the curves can be evaluated with highest relative accuracy is selected. The relative times required for conversion to a given percentage of naphthalene are the reciprocals of the relative rates, and they are equal to the kinetic isotope effects as conventionally expressed $(k_{\rm H}/k_{\rm D})$. Table I shows the results extracted from Figure 1. Corrected for isotopic purity, the effects for tetralin-1,1,4,4-d₄, -2,2,3,3-d₄, and $-d_{12}$ are 2.0, 2.0, and 3.7. Previously¹⁷ we reported a value of 2.1 for tetralin- $1, 1, 4, 4-d_4$. These values conform surprisingly well to the pattern expected for concerted (pericyclic) hydrogen transfer. On the basis of IR stretching frequencies for C-H and C-D in tetralin we calculate a maximum "ordinary" effect of 2.5 for transfer of a single hydrogen at 335 °C.

There afe, of course, many reports of anomalous isotope effects in the literature including tunneling¹⁹ and temperature-independent effects.²⁰ We are unable to devise a practical experiment which would admit or exclude such "wild cards". The results would have a trivial explanation if tetralin should exchange hydrogen under the reaction conditions. Such exchange has been reported at higher temperatures,²¹ but we have found no measurable loss of deuterium from unreacted tetralin recovered after extensive reaction with coal at 335 °C. The results would be

⁽¹⁰⁾ Poutsma, M. L.; Dyer, C. W. J. Org. Chem. 1982, 47, 4903.

⁽¹¹⁾ Gilbert, K. E. J. Org. Chem. 1984, 49, 6. (12) Ross, D. S.; Blessing, J. E. Fuel 1979, 58, 433

⁽¹³⁾ Virk, P. S. Fuel 1979, 58, 149.

⁽¹⁴⁾ Virk, P. S.; Bass, D. N.; Eppig, C. P.; Ekpenyong, D. J. Prepr. Div. Fuel Chem., Am. Chem. Soc. 1979, 24 (2) 144. (15) King, H.; Stock, L. M. Fuel 1981, 60, 748.

⁽¹⁹⁾ Melander, L.; Saunders, Jr., W. H. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980; p 140. (20) Kwart, H. Acc. Chem. Res. 1982, 15, 401. (21) King, H.; Stock, L. M. Fuel 1982, 61, 257.



Figure 2. Reaction of coal with 1,2-dihydronaphthalene. Percent naphthalene vs. time in hours.

consistent with rate-controlling loss of a single hydrogen from the α -position provided that both the primary and secondary kinetic isotope effects have a value of 2. Such a large secondary effect has not been reported previously, and the value is typically 1.1 at ordinary temperature (1.05 adjusted to high temperature) for $S_N 1$ reactions in which the isotope is directly connected to the reacting carbon atom. In one study involving free radicals²² the secondary effect at β -carbon was 1.08 per D atom, but ordinarily the value is lower. Another way in which the results could be reconciled with stepwise reaction is to assume that the primary effect has a value of 3.7 and that there is no selectivity between α - and β -positions. The value of 2.0 for α -deuterated and β -deuterated tetralin would then result from dilution by reaction at unlabeled positions. The evidence against this assumption is very strong. A primary effect greater than 2.5 could only result from tunneling or some even stranger anomaly. Furthermore there is direct evidence of selectivity in favor of the α -position in the high-temperature exchange mentioned earlier.²¹ The reaction of chlorine atoms with isobutane is better characterized, and it shows a selectivity ratio of 5.23 Ultimately it seems to be the most believable conclusion that transfer of hydrogen atoms from the two positions is concerted.

Even if it should be found in the future that the reaction is not really pericyclic, the peculiar pattern of isotope effects could serve a diagnostic purpose. It is shown below that the pattern is different for 1,2-dihydronaphthalene, and in a planned sequel to this report it is shown to be similar for some model substrates and different for others. A similar pattern is strong evidence for a similar mechanism, and there are better opportunities to clarify the details by using model compounds rather than coal.

1,2-Dihydronaphthalene. The dihydronaphthalenes are much more reactive than tetralin, and it was necessary to lower the temperature to 220 °C in order to moderate the reaction for convenient rate measurements. 1,4-Dihydronaphthalene was not used for several reasons including analytical difficulties, problems in synthesis of the 1,1-dideuterio derivative, and necessity for excluding possible base-catalyzed rearrangement to 1,2-dihydronaphthalene in the presence of coal minerals. Except for



Figure 3. Reaction of coal with 1,2-dihydronaphthalene. $\ln k (s^{-1}) \times 10^5$ vs. pressure (MPa).

Table II. Relative Reaction Times for Deuterated Dialins

% C ₁₀ H ₈	d_0	d_{10}	1,1,3-d ₃	_
8	(1.0)	2.6	1.11	-
10	(1.0)	2.8	1.13	
12	(1.0)	2.7	1.10	

Table III. Effect of Pressure on Rate of Reaction of 1,2-Dihydronaphthalene with Coal at 210 °C

pressure, MPA	34.5	69.0	103.4	
1st-order rate constant $(s^{-1}) \times 10^5$	4.58	5.47	6.50	
Scheme II				



the temperature difference, the reaction conditions and procedure resembled those for tetralin. Results are shown in Figure 2 and Table II.

Even at a significantly lower temperature the kinetic isotope effect for perdeuterated 1,2-dihydronaphthalene is only 2.7 in comparison to the value of 3.7 obtained for tetralin. The 1,1,3-trideuterio derivative has an isotope effect of only 1.1 which would appear to be a β -secondary effect. Evidently there is a fundamental difference in mechanism between tetralin and 1,2-dihydronaphthalene in that the latter undergoes rate-controlling loss of a single hydrogen from the 2-position. The intermediate could be either a radical or a cation.

These kinetic isotope effects are very similar to the findings of another study involving the reaction of tetracyanoethylene with $1,1-d_2, 2,2-d_2$, cis- $1,2-d_2$, and trans- $1,2-d_2$ derivatives of 1,2-dihydronaphthalene.²⁴ For $1,1-d_2$ the effect was 1.1 and for $2,2-d_2$ it was 2.8. The results were interpreted to indicate transfer of hydride ion from the 2-position as the rate-controlling step. Although the cisand trans- $1,2-d_2$ compounds showed considerable stereo-specificity, the isotope effect (2.5) indicated stepwise rather than concerted hydrogen transfer. Scheme II was proposed to accomodate the observations.

Activation Volume for 1,2-Dihydronaphthalene. The reaction of 1,2-dihydronaphthalene with coal was

⁽²²⁾ Tsolis, A.; Hunt, P. P.; Kochi, J. K.; Seltzer, S. J. Am. Chem. Soc. 1976, 98, 992.

⁽²³⁾ Pryor, W. A. "Introduction to Free Radical Chemistry"; Prentice-Hall: Englewood Cliffs, NJ, 1966; p 53.

⁽²⁴⁾ Heesing, A.; Mullers, W. Chem. Ber. 1980, 113, 24.

followed at several pressures up to 103 MPa using the same apparatus, procedures, and methods of data reduction as previously reported for the reaction of coal with tetralin.¹⁷ Table III gives the rate constants for the various pressures and Figure 3 is a plot of the logarithm of the rate constant vs. P from which we calculate an activation volume of -23 ± 3 mL/mol. This is nearly the same as the value of -27mL which was given by tetralin. It indicates that the rate-controlling step is bimolecular, but does not distinguish between pericyclic and other bimolecular mechanisms. Reactions which are known to be pericyclic such as the Diels-Alder reaction are characterized by activation volumes from -20 to -40 mL.²⁵ The only mechanism which can be completely excluded is the one analogous to Scheme I. Note that dihydronaphthalene is implied as an intermediate in Scheme I.

Experimental Section

Naphthalene- d_8 . This compound which was needed for the preparation of tetralin- d_{12} and tetralin- $2,2,3,3-d_4$ was obtained by acid-catalyzed exchange between naphthalene and D₂O. A mixture of 0.6 mL of POCl₃, 6 mL of D₂O, and 6 g of naphthalene was sealed in a glass tube having 25 mL capacity. The tube was heated in a pressure vessel for 1 h at 300 °C under 17 MPa of external pressure to prevent bursting. The partially deuterated naphthalene was isolated by filtration, and the procedure was repeated several more times until 98% of the hydrogen was replaced by deuterium as indicated by IR and NMR measurement. The final product was purified by distillation, bp 212 °C (650 torr).

Tetralin- d_{12} . Deuterium gas was generated by electrolysis of D_2O with Na_2CO_3 electrolyte and pumped into a 100-mL pressure vessel containing 18 g of naphthalene- d_8 and 1 g of 10% Pd on C catalyst to a final pressure of 2.3 MPa. The reactor was heated to 100 °C and shaken for several hours until most of the D_2 was consumed. The procedure was repeated 3 times until the theoretical quantity of D_2 was taken up. The product was filtered and distilled through a fractionating column, bp 198-199 °C (650 MPa). Analysis by IR and density indicated 93% D. The electrolysis step is probably responsible for most of the admixture of H.

Tetralin-1,1,4,4- d_4 . The base-catalyzed exchange of D_2O with tetralin was used as described previously.¹⁷

Tetralin-2,2,3,3-d₄. Tetralin- d_{12} was exchanged with H₂O and base by the same procedure used for tetralin-1,1,4,4, except that a large quantity of water was used in a single-step exchange. The 2- and 3-positions remained 93% deuterated. Most of the deuterium was removed from the aromatic ring as well as the 1- and 4-positions.

1,2-Dihydronaphthalene. A solution of 10 g of naphthalene in 200 mL of anhydrous ethanol was placed in a 500-mL flask equipped with a magnetic stirrer and reflux condenser. Sodium

(25) Asano, T.; le Noble, W. J. Chem. Rev. 1978, 407.

metal (16.6 g) was added in small pieces over a period of 2 h. The reaction mixture was then heated at 170 °C for 3 h in a pressure vessel in order to convert 1,4-dihydronaphthalene into 1,2-dihydronaphthalene. The mixture was then neutralized with 40 mL of acetic acid, and most of the ethanol was removed by distillation. The organic layer was taken up in ether, dried, and distilled to give 66 g, bp 202 °C (650 torr). The product contained 8% of unrearranged 1,4-dihydronaphthalene.

1,2-Dihydronaphthalene- d_{10} . The procedure above was applied to naphthalene- d_8 using EtOD and CH₃CO₂D in place of EtOH and CH₃CO₂H. From 7.5 g of deuterated naphthalene we obtained 5 g of product containing 94% D.

1,2-Dihydronaphthalene-1,1,3- d_3 . A mixture of 20 mL of α -tetralone, 20 mL of D₂O, and 1 g of NaOD was heated in a pressure vessel for 5 h at 250 °C. The procedure was repeated several times until replacement of H by D at the 2- and 4-positions was 98% complete as indicated by NMR. This yielded 18 mL of deuterated tetralone which was added to a solution of 4 g of NaBH₄ in 30 mL of MeOH at room temperature. After several hours the mixture was acidified with acetic acid, and the deuterated α -tetralol was removed by partition between water and ether. The ether layer was dried, evaporated to remove ether, and heated for 30 min at 140 °C with 1.5 g of CuSO₄ catalyst in order to dehydrate the tetralol to 1,2-dihydronaphthalene. Distillation through a fractionating column gave 11 g of product, bp 196-198 °C (650 torr), which contained less than 5% H at the 1-position.

Coal Sample. The New Mexico Bureau of Mines and Mineral Resources, a Division of this Institute, supplied a sample of subbituminous coal from the Navajo Mine of the Utah International Coal Company. The elemental analysis of the coal as received: C, 54.8; H, 5.6; O, 22.2; N, 1.0; S, 0.7; ash, 15.7.

Apparatus, Procedures, and Analysis. The preparation, containment, heating, pressurization, and analysis of reaction mixtures has been previously described.^{17,28} The only significant change in the analysis is the use of a Tracor 565 capillary GC to determine the proportions of naphthalene and hydrogen donor. Again we note the absence of any other peaks for compounds boiling as high as anthracene and can assert that tetralin pyrolysis products such as hydrogen, decalin, 1-methylindan, butylbenzene, ethylbenzene, toluene, etc. are not formed in detectable quantity.

Rate Equation and Activation Volume. The extraction of rates and activation volumes from the data have been previous described.¹⁷

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Registry No. Tetralin, 119-64-2; 1,2-dihydronaphthalene, 447-53-0; naphthalene- d_8 , 1146-65-2; tetralin- d_{12} , 75840-23-2; tetralin-2,2,3,3- d_4 , 91780-99-3; 1,2-dihydronaphthalene- d_{10} , 91781-00-9; 1,2-dihydronaphthalene-1,1,3- d_3 , 91781-01-0; deuterium, 7782-39-0.

(26) Brower, K. R. J. Org. Chem. 1980, 45, 1004.