20%); mp 180–181 °C (from $CHCl_3$–petroleum ether); NMR δ 2.2 (s, 3, $CH_3C_6H_4$) 6.7–7.8 (m, 12, Ar H, OH, NH); IR (Nujol) 3320 and 3280 cm^{-1}.

Rearrangement of 17a to 17b. Sulfonamide **17a** (300 mg, 0.108 mmol) in THF (50 mL) was treated with *n*-BuLi (4 mL, 6.4 mmol) at −68 °C for 2 h and then at room temperature for 0.5 h. The solution went from yellow to dark red. After hydrolysis, the major product (**17b**) was isolated by preparative TLC (SiO_2, 9:1 CH_2Cl_2/EtOAc): 50 mg (0.018 mmol, 17%); mp 119–120 °C (from EtOH); NMR δ 2.4 (s, 3, $CH_3C_6H_4$), 2.8 (s, 3, NCH_3), 6.5–7.8 (m, 10, Ar H, NH). IR (Nujol) 3420 (NH), 3260 (NH) cm^{-1}.

Attempted Thermal Rearrangement of 1a. (a) A sample of sulfonate **1a** in a melting point capillary tube was kept at 197 °C for 0.5 h during which time the clear melt became dark in color. Analysis of the melt by TLC revealed no sulfonamide **1b**. (b) A solution of sulfonate **1a** (200 mg) in diglyme (20 mL) was heated under reflux under a nitrogen atmosphere for 6 h. Upon removal of the solvent, only starting material was detected by TLC. No sulfonamide **1b** was observed.

Crossover Experiment. Sulfonates **2a** (1.5 g, 5.4 mmol) and **6a** (1.5 g, 4.7 mmol) in THF (800 mL) cooled to 0 °C were treated with *n*-BuLi (1.6 M, 26 mL, 42 mmol). After being stirred for 6 h at room temperature, the mixture was hydrolyzed with 5% HCl (100 mL), concentrated in vacuo, and extracted with ether. The ether extracts were analyzed by a combination of column chromatography, TLC, and NMR. Sulfonamides **2b** and **6b** were shown to be present whereas **3b** and **5b** were absent. There was no spot for **3b** on TLC. Sulfonamide **5b** shown to be absent by adding authentic samples to fractions from the column chromatography. A signal at δ 2.14 due to the 5′-CH_3 group of **5b** was absent in the fraction which contained **6b** (5′-Me at δ 2.08).

Rearrangement of 8a to 8b. Sulfonate **8a** (2.4 g, 7.87 mmol) in THF (150 mL) was treated with *n*-BuLi (15 mL. 27 mmol) for 0.5 h at −78 °C and then for 2.5 h at room temperature. After the usual workup sulfonamide **8b** was isolated: 100 mg (0.32 mmol, 42%); mp 129–130 °C. 2,2′-Dihydroxy-5,5′dimethylazobenzene (**12**) was also isolated: 200 mg (0.83 mmol, 11%); mp 216–217 °C (lit.[23] mp 216–217 °C); MS *m/e* 242; ^1H NMR δ2.3 (s, 6, CH_3), 6.8–7.5 (ABC m, 6, Ar H), (s, 2, OH); ^{13}C NMR δ 20.4, 118.6, 130.2, 131.3, 134.5, 135.6, 151.2; IR (KBr) 3430 (OH) cm^1.

Rearrangement of 8a to 8b in the Presence of Sodium *p*-Toluenesulfinate. A mixture of **8a** (250 mg, 0.82 mmol), anhydrous sodium *p*-toluenesulfinate (500 mg, 2.76 mmol), and THF (80 mL) was treated with *n*-BuLi (2.0 mL, 3.3 mmol) as above. The workup of the reaction mixture gave results as above with no evidence (TLC) for the presence of **4b**.

Treatment of 2-Hydroxyphenyl Benzenesulfonate (21) with *n*-BuLi. Sulfonate **21** (250 mg, 1 mmol) in THF (25 mL) was treated with *n*-BuLi (0.63 mL, 1.0 mmol) at −78 °C for 0.5 h and then at room temperature for 3 h. The solution remained colorless. Starting material **21**, as indicated by TLC and NMR, was recovered quantitatively upon hydrolysis of the reaction mixture.

Reaction of *p*-Toluidine (26) with Phenyl *p*-Toluenesulfonate (27). *p*-Toluidine (495 mg, 0.42 mmol) in THF (25 mL), cooled to −68 °C, was treated with MeLi (10 mL, 12.5 mmol) whereupon the solution turned pale yellow. Sulfonate **27** (1.1 g, 0.44 mmol) was added. After 1.5 h, the mixture was brought to room temperature whereupon the color turned to dark red. After 0.5 h, the mixture was hydrolyzed and worked up as usual. TLC revealed no starting material nor any *N*-(4-tolyl)-4-toluenesulfonamide. The products were not further investigated.

Reaction of 4-Aminophenyl 4-Toluenesulfonate (29) with *n*-BuLi. Sulfonate **29** (500 mg, 1.9 mmol) was treated with MeLi (5.4 mL, 7.6 mmol) in THF (100 mL) at 0 °C. Upon the usual workup, the reaction mixture became dark purple during solvent removal. Repetitions of the reaction always resulted in dark-colored materials which were not futher identified.

Acknowledgment. We thank the NSF for partial support of this research and for providing funds for the purchase of a JEOL FX90Q spectrometer (Grant No. CHE-77893). We also thank M. Turnbull for experimental assistance.

Registry No. 1a, 1216-96-2; **1b**, 3897-39-0; **2a**, 81256-07-7; **2b**, 81256-08-8; **3a**, 81278-80-0; **3b**, 81256-09-9; **4a**, 81256-10-2; **4b**, 81256-11-3; **5a**, 81256-12-4; **5b**, 81256-13-5; **6a**, 81256-14-6; **6b**, 81256-15-7; **7a**, 81256-16-8; **7b**, 81256-17-9; **8a**, 81256-18-0; **8b**, 81256-19-1; **13**, 81256-20-4; **14a**, 30378-30-4; **14b**, 81256-21-5; **15a**, 81256-22-6; **15b**, 81256-23-7; **16a**, 81256-24-8; **16b**, 36364-83-7; **17a**, 25446-46-2; **17b**, 38163-84-7; **21**, 3839-96-1; **26**, 106-49-0; **27**, 640-60-8; **29**, 3899-93-2; 2-aminophenol, 95-55-6; 8-aminonaphthol, 2834-91-5.

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Effects of Pressure and Isotopic Substitution on the Rate of Reaction of Coal with Tetralin

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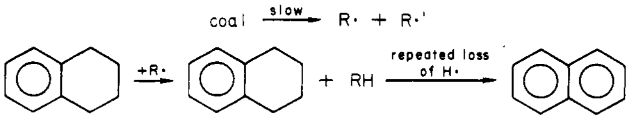
The molar activation volume for the reaction of coal with tetralin at 344 °C is −27 ± 3 mL. This result suggests a transition state which is bimolecular and possibly ionic. It is inconsistent with the hypothesis that the rate is controlled by homolysis of the coal molecule. The H/D kinetic isotope effect for the reaction of coal with tetralin containing deuterium at the α-positions is 2.1 ± 0.1 at 335 °C. This result reinforces the conclusions based on the activation volume.

Since 1967 a majority of writers on the subject of liquefaction of coal by hydrogen donor solvents have endorsed the free-radical mechanism proposed by Curran, Struck, and Gorin.[1] The rate-limiting step is assumed to be homolysis of a C–C or C–O bond followed by abstraction of hydrogen atoms from the donor. Using tetralin as an example of a donor solvent, one may represent the process as in Scheme I. Following this proposal there have been a number of studies of the free-radical decomposition of

Scheme I



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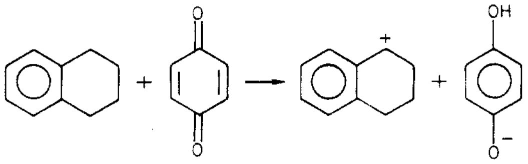
(1) G. P. Curran, R. T. Struck, and E. Gorin, *Ind. Eng. Chem. Process Des. Dev.*, **6**, 166 (1967).

0022-3263/82/1947-1889$01.25/0 © 1982 American Chemical Society

Scheme II



model hydrocarbons in the presence of tetralin.[2-8] Careful reading of the literature discloses that few if any of the model compounds which react by undisputed radical pathways are as reactive as coal even though they are often selected to yield unusually stable radicals. The half-life of dibenzyl in tetralin at 400 °C is reported to be 10.5 h,[4] in fair agreement with a value of 12.3 h obtained in our laboratory.[9] The reaction of coal under the same conditions is too rapid for convenient measurement. Dibenzyl ether is almost as reactive as coal, but it has been found that the toluene which it yields as a product is formed largely by an intramolecular pathway.[4] It is conceivable and even likely that coal forms small amounts of stabilized radicals which then react with tetralin in a second-order process. The bulk of the reaction probably does not proceed in this way because the redox equivalent weight of subbituminous coal lies in the range of 60–100 (dry ash-free basis),[10] and it is difficult to imagine a structure for radical fragments of such light weight and high stability. The low equivalent weight is compatible, however, with the reaction schemes discussed below.

Aside from the hydrogenolysis of C–C and C–O bonds, the reduction of carbonyl groups could play an important role in coal liquefaction.[10] Although carbonyl reduction has little effect on molecular weight or size, it can greatly reduce the solubility parameter. Anthraquinone, for example, is reduced by tetralin at 400 °C to anthracene which is much more soluble in hydrocarbons than anthraquinone. The aromatization of tetralin and related compounds by active quinones such as *o*-chloranil and 2,3-dichloro-5,6-dicyanoquinone is a known synthetic procedure.[11,12] There is evidence in favor of an ionic mechanism involving bimolecular transfer of a hydride ion from tetralin to the quinone.[12] The rate-controlling step is shown in Scheme II.

Donation of hydrogen to coal has recently been achieved by base-catalyzed reaction with 2-propanol. Ross[13] proposes a hydride-transfer mechanism in analogy to the Meerwein–Ponndorf–Verley reduction. He also suggests the possibility of displacement by hydride ion of an ether group from a sensitive position such as the 9-position of anthracene. This would not only lower the solubility parameter but would also reduce the molecular weight.

A third possible mechanism is the pericyclic pathway proposed by Virk, Bass, Eppig, and Ekpenyong.[14] They have demonstrated a specificity dictated by symmetry rules in the transfer of hydrogen from the dihydronaphthalenes to anthracene and phenanthrene. With tetralin, however, these substrates are much less reactive than coal. Conceivably, substituent effects in coal could enhance the acceptor reactivity to the point where rate-controlling pericyclic reaction with tetralin would be fast enough to agree with observation. It is also possible that the pericyclic pathway operates only in transferring the second mole of hydrogen in the stepwise conversion of tetralin to naphthalene via 1,2- or 1,4-dihydronaphthalene.

On the assumption that the slow step in coal reduction is dominated by a single broad type of process, e.g., homolysis, hydride transfer, or pericyclic group transfer, we believe it is useful to measure the H/D kinetic isotope effect using deuterated tetralin. The very existence of an effect would be inconsistent with the concept of rate-controlling homolytic initiation since tetralin would not be a moiety of the transition state. Substantial isotope effects have been observed for the reaction of tetralin with a quinone[12] and for hydride transfers from other donors.[15] We have found no record of measured isotope effects for the pericyclic group transfer, but a substantial effect has been predicted.[16] For the last two mechanisms we have no grounds for predicting which would have a larger effect.

Another useful mechanistic tool is the activation volume derived from measurement of the effect of pressure on rate. Details of the method and the principles of interpretation may be found in a recent review.[17] The method of activation volumes is especially well suited to a reaction which cannot be described in detail since it has no specific relation to functional classification, stereochemistry, orbital hydridization, or even elemental composition. Briefly stated the principles are as follows. (1) Bond breaking in the transition state increases the volume from approximately 10 mL at ordinary temperature to 30 mL at high temperature. (2) Contrariwise, bond making causes a decrease in volume. (3) Ionization decreases the volume by electrostriction of the medium. If unimolecular free-radical decomposition of coal is the slow step, the reaction should be retarded by pressure since the activation volumes for the reactions of this type have been positive in every reported case.[17] Reactions in which bimolecular hydride transfer is rate controlling have negative activation volumes.[18] The closest models for the pericyclic group transfer are cycloaddition reactions of neutral molecules which invariably have negative activation volumes.[17]

Results and Discussion

For both the isotope effect and the pressure effect the reaction was followed by measuring the rate of change of the molar ratio of naphthalene to tetralin. It has been reported that tetralin alone or admixed with other substances can isomerize to 1-methylindan and disproportionate to naphthalene, decalin, and other substances.[19] We were careful, therefore, to establish that the temperatures and times used in our study were such that the

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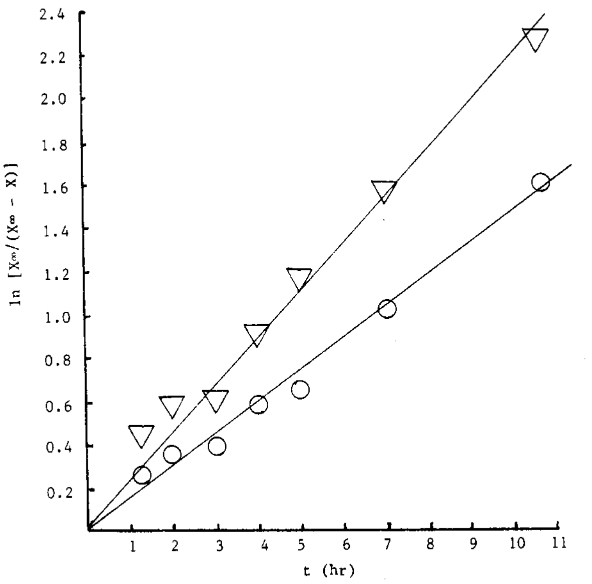

Figure 1. Reaction of coal B with tetralin: circles, D; triangles, H.

Table I. Activation Volumes for Reaction with Tetralin

reactant	temp, °C	ΔV^*, mL/mol
bibenzyl[9]	395	31 ± 3
thymoquinone	175	−28 ± 3
coal sample A	344	−27 ± 3

naphthalene/tetralin ratio was essentially stationary at 10 half-lives and that decalin and 1-methylindan were not formed in significant amounts. A factor of possible significance is that our reaction mixtures were contained in all-glass cells.

Figure 1 is a plot of the natural logarithm of the fraction of completion of conversion of tetralin to naphthalene vs. the time in hours. The first-order rate law gives a reasonable fit over a range of 2–3 half-lives. After correction for isotopic purity, the isotope effect (k_H/k_D) is 2.1. A value of 2.45 was calculated for the upper limit of the isotope effect at 608 K by using the measured IR frequencies of the appropriate bands in deuterated and undeuterated tetralin: 2090, 2180 cm^{-1} (D); 2900 cm^{-1} (H). The effect is so pronounced that it seems to be inconsistent with the widely held belief that homolysis of coal molecules is rate controlling. Both hydride ion transfer and pericyclic group transfer remain as possible mechanisms, and it is not clear that one can be favored over the other. Ordinary reactions via hydride ion transfer have isotope effects considerably below the maximum, but the high reaction temperature (608 K) could result in a looser transition state. Simultaneous transfer of two hydrogen atoms by the pericyclic mechanism could have a higher upper limit (6.0), but our tetralin was deuterated only at the α-positions. Transfer from two α-positions (a $4n + 2$ system) is permitted with an acceptor such as anthracene (a $4n$ system) but would be highly endothermic with respect to transfer from the α- and β-positions.

Activation volumes for the reaction of coal with tetralin and two model reactions are given in Table I. The coal reaction is clearly more similar to the reduction of thymoquinone which is thought to proceed by transfer of a hydride ion as shown above in Scheme II. The contrast to the homolytic decomposition of bibenzyl is striking. Thymoquinone was chosen as a model in preference to the previously studied quinones with chloro and cyano substituents because deactivating substituents such as alkyl groups are expected to prevail in coal. The alkyl groups also promote miscibility with tetralin and permit the concentration to be high enough for reliable analysis. The reaction of tetralin with coal differs so much from the relatively simple homogeneous reactions of model compounds that some thought should be given to the possibility that the effects of pressure on transport processes and phase equilibria are obscuring the effect on the concentration of activated complexes. There are several reasons for thinking that transport between phases does not limit the rate: (1) Transport would show a negligible isotope effect. (2) Fineness of subdivision of the coal does not affect the rate. (3) Fluidity and diffusivity are always reduced by pressure whereas we find that the reaction rate is increased. (4) The temperature coefficient and "activation energy" for transport processes are much too small to fit our observations. Pressure would affect the equilibrium distribution of tetralin between phases to the extent that there is a volume change on transfer. The two phases which form the principal reservoirs of tetralin are the homogeneous liquid phase which consists chiefly of tetralin by weight and the coal phase which is swollen by tetralin and coal liquids. In the vast literature on excess mixing volumes of organic liquids one seldom finds a value exceeding 1 mL/mol, and there is no consistency of sign. There is, consequently, no reason to think that pressure would squeeze the tetralin into or out of the reaction phase to a significant extent.

It is conceivable that radicals can be formed by a bimolecular process for which a negative activation volume would be expected. A reaction which has been claimed to have this mechanism is the pyrolysis of cyclohexa-1,3-diene.[20] If the reaction of coal with tetralin were to follow this path, the negative activation volume would be appropriate. If the radicals were generated by coal alone, there would be no kinetic isotope effect, but the case would be different if tetralin were one of the components of the disproportionation. We cannot rule out this mechanism although the conditions seem rather restrictive. As we have noted earlier, tetralin does not react with itself or the liquids derived from coal under our experimental conditions.

If coal were to react with tetralin by way of low-energy coal radicals whose formation is not rate-determining, there would be no net change in the number of bonds between the initial state and the transition state. The predicted activation volume would be zero. There would, however, be an isotope effect.

The apparent activation energy for the reaction of coal with tetralin was measured in conjunction with the determination of the isotope effect and was found to be 160 kJ. This parameter is less useful than the activation volume as a criterion of mechanism, but it does permit one interesting inference. If the reaction is bimolecular, the entropy of activation cannot be evaluated unless the rate constant can be expressed in standard concentration units, which we are unable to do, but if it is unimolecular, the difficulty is removed. Under this assumption the activation entropy is −19 eu. This large negative value is clearly inappropriate for a radical decomposition. A value of 9 eu was found for the pyrolysis of bibenzyl.[9]

Experimental Section

Deuteration of Tetralin. A mixture of 20 mL of tetralin, 20 mL of D_2O, and 1 g of NaOD was heated in a well-seasoned stainless-steel pressure vessel of 90-mL capacity for 1 h at 370 °C. Analysis of the organic layer by NMR indicated 48% deu-

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Table II. Rate Data for Reactions with Tetralin

Thymoquinone at 175 °C							
P, MPa	3.3	20.0	33.3	66.5q	99.9	133.0	
$10^5 k$, s^{-1}	1.90	2.20	2.49	2.80	3.84	5.18	
Coal Sample A at 344 °C (6.7 MPa)							
X	0.10	0.15	0.20	0.26	$k \simeq 1.42 \times 10^{-4}$		
$10^{-3} t$, s	3.6	6.0	12.0	48.0			
Coal Sample A at 344 °C (93.3 MPa)							
X	0.14	0.18	0.24	0.26	$k \simeq 2.08 \times 10^{-4}$		
$10^{-3} t$, s	3.6	6.0	12.0	30.0			
Coal Sample B at 335 °C (3 MPa). Tabulation of $\ln [X/(X_\infty - X)]$ with (D) and without (H) Deuterium							
F(X): D	0.292	0.365	0.400	0.505	0.665	1.04	1.60
H	0.416	0.549	0.596	0.904	1.17	1.55	2.25
$10^{-4} t$, s	0.45	0.72	1.08	1.44	1.80	2.52	3.82

teration at the α-position and 29% deuterated on the benzene ring. There was no indication of exchange at the β-position. Analysis by GC showed less than 1% conversion to naphthalene. Repetition several times with a countercurrent procedure eventually produced 40 mL of tetralin which was 90% deuterated at the α-position and 61% deuterated on the benzene ring. When NaOD was omitted, there was no exchange at any position. Final purification was effected by distillation through a fractionating column; bp 195–196 °C (650 mmHg). The IR spectrum showed C–D stretching bands at 2090 and 2180 cm^{-1}.

Preparation of Thymoquinone. The procedure of Kermers, Wakeman, and Hixon was used without modification.[21]

Coal Samples. The New Mexico Bureau of Mines and Mineral Resources, a Division of this Institute, supplied samples of subbituminous coal from the Navajo Mine of the Utah International Coal Co. Sufficient coal for a series of rate runs was pulverized and stored under vacuum.

Preparation and Containment of Samples. Reaction mixtures were prepared by mixing 1 g of pulverized coal with 1 g of tetralin. For measurement of the isotope effect, the samples were sealed in borosilicate glass tubes having a 3-mL capacity. For prevention of bursting, the tubes were externally pressurized to 10 MPa. The internal pressure was probably 3–4 MPa.

For measurement of the pressure effect the samples were placed in a 5-mL borosilicate glass syringe having a test tube end in place of the original tip. The top of the plunger was sawed off, and the plunger was inserted in the barrel under reduced pressure.

Thymoquinone was treated like coal except that 0.5 g was used rather than 1 g.

Workup and Analysis of Reaction Mixtures. Partially reacted mixtures were removed from the sealed tube or syringe and transferred to a steam distillation apparatus. After 15 mL of steam distillate had been collected, the organic portion was extracted with ether, dried with $MgSO_4$, and concentrated to a small volume. A 10-μL portion of the residue was injected in a gas chromatograph, and a combined fraction embracing the tetralin and naphthalene peaks was collected. Although these peaks were almost completely resolved, the integals did not give as good reproducibility and accuracy as the following method. The combined fraction (approximately 4 mg) was weighed, dissolved in hexane, and diluted to 25 mL. The solution was diluted further as required to give an absorbance near 0.3 in a 1-cm cell at 280 nm where naphthalene absorbs strongly but tetralin does not. The composition was read from a graph obtained by use of known mixtures. The relative error was about 5% for mixtures containing 10% by weight of naphthalene.

Several GC fractions were collected over a wide range which would embrace not only tetralin and naphthalene but also the decalins and 1- or 2-methylindan for which peaks were not visible above the noise. The aliphatic region of the NMR spectrum showed only absorption by tetralin. By trial it was found that 1-methylindan could have been detected at the 1% level.

Apparatus and Reaction Procedure. The high-pressure equipment and heating device were the same as those used in a previous study of the pyrolysis of bibenzyl.[9] The method of adjusting the time scale to allow for the time of temperature rise was also the same.

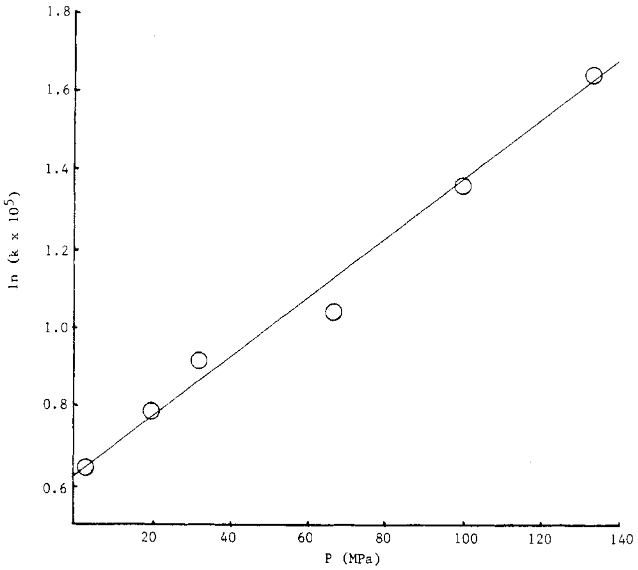

Figure 2. Reaction of thymoquinone with tetralin.

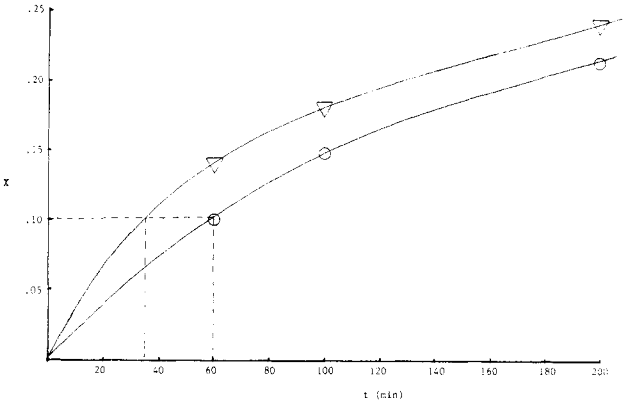

Figure 3. Reaction of coal A with tetralin; circles, 6.7 MPa; triangles, 93.3 MPa. X = weight fraction of naphthalene in the stream distillate.

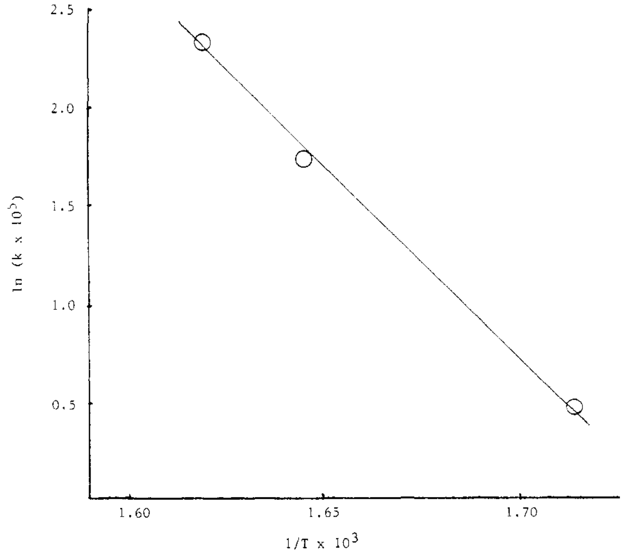

Figure 4. Reaction of coal B with tetralin.

Rate Laws. The reaction of tetralin with quinones is second order,[11,12] but our reaction with thymoquinone was carried out under pseudounimolecular conditions with an excess of tetralin. With *X* = weight fraction of naphthalene in the stream distillate

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[21] E. Kremers, N. Wakeman, and R. M. Hixon, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 511.

after time t, and $X_\infty = 0.215$, we evaluated the rate constant, k, from the expression $\ln [X_\infty/(X_\infty - X)] = kt$.

It is not reasonable to expect a rate law of pure type for such a nondescript substance as coal, but a pseudo-first-order treatment fits the data reasonably well as shown in Figure 1. The value of X_∞ is not available from stoichiometry and must be determined by experiment. At 10 half-lives the values are 0.265 for coal sample A at 344 °C, 0.260 for coal sample B at 335 °C, and 0.268 for coal sample B with deuterated tetralin at 335 °C. Pseudounimolecular rate constants are shown in Table II.

Evaluation of Activation Volume. The activation volume, ΔV^*, is obtained from a plot of ln k vs. P according to eq 1. Figure

$$-RT(\delta \ln k/\delta P)_T = \Delta V^* \qquad (1)$$

2 presents the results for the reaction of thymoquinone with tetralin at 175 °C.

Fortunately, it is possible to obtain a meaningful ΔV^* even though the rate law for the reaction is unknown. Figure 3 pertains to the procedure applied to the reaction of coal sample A with tetralin. Let the integrated form of the unknown rate law be represented as $F(X) = kt$. On the assumption that only k is a function of P, the pressure effect (k_P/k_0 = ratio of rate constants at high and low pressure) at constant X is equal to t_0/t_P. We than use the relation shown in eq 2. Some values of k_P/k_0 obtained

$$-RT(\ln k_P/k^0)\Delta P = \Delta V^* \qquad (2)$$

graphically from smooth lines drawn through the measured points are 1.68 ($X = 0.09$), 1.62 ($X = 0.10$), 1.58 ($X = 0.12$), and 1.50 ($X = 0.14$). Substitution in the preceding equation gives $\Delta V^* = -26.7 \pm 2.0$ mL.

Apparent Activation Energy. Values of the pseudo-first-order rate constant for the reaction of coal sample B with tetralin at autogenic pressure in reciprocal hours are 0.058 at 310 °C, 0.212 at 335 °C, and 0.369 at 345 °C. A graph of ln k vs. $1/T$ gives ΔE^* = 38 kcal (160 kJ) as shown in Figure 4.

Acknowledgment. This work was supported by U.S. Department of the Interior (Grant G-5104024).

Registry No. Tetralin, 119-64-2; thymoquinone, 490-91-5.

Further Studies of Substitution Reactions of Stannyl and Germyl Anionoids with Alkyl Bromides. Rearrangement of the 6-Hepten-2-yl Moiety[1]

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The stereochemical outcomes of reactions of (trimethyltin)lithium, (dimethylphenyltin)lithium, (methyldiphenyltin)lithium, and (triphenyltin)lithium in tetrahydrofuran with *trans*- and *cis*-2-, 3-, and 4-methylcyclohexyl bromides have been determined on the basis of ^{1}H and ^{13}C NMR spectroscopy. The $(C_6H_5)_3SnLi$ reactions proceed stereospecifically with inversion at carbon, while the $(CH_3)_3SnLi$ reactions are nonstereospecific, as observed previously in some other systems. *cis*- and *trans*-2-methoxybromocyclohexanes and -cyclopentanes were also reacted with $(CH_3)_3SnLi$, and low yields of (2-methoxycyclohexyl)- and (2-methoxycyclopentyl)trimethylstannanes were isolated. On the basis of ^{13}C NMR spectra and deoxystannylation reactions, the former is largely (~90%) trans while the latter is exclusively trans. The pronounced stereochemical distinction between reactions of $(CH_3)_3SnLi$ and $(C_6H_5)_3SnLi$ with cyclohexyl bromides is not observed in corresponding reactions of $(CH_3)_3GeLi$ and $(C_6H_5)_3GeLi$; both are nonspecific. Certain reactions of cyclopropylcarbinyl bromide and 6-bromo-1-hexene with R_3SnLi and R_3GeLi ($R = CH_3$ or C_6H_5) were also studied. Rearranged product (allylcarbinyl) was observed in the reaction of cyclopropylcarbinyl bromide with $(CH_3)_3SnLi$, but cyclopentylmethyl products (from cyclization of any hex-5-enyl free radical) was not observed in any case. However, with the secondary 6-bromo-1-heptene all reagents studied (with the exception of $(C_6H_5)_3SnLi$) afforded rearranged (2-methylcyclopentyl)methyl products, consistent with the intervention of the free radical, which cyclizes rapidly. Some further estimates of the conformational A values of R_3Ge and R_3Sn are reported, and the triphenyl derivatives have significantly larger values.

The reactions of alkyl bromides with triorganotin or germylalkali reagents are useful for synthesis of the tetraorganometallics, e.g., eq 1. The stereochemical and other

$$RBr + R'_3SnM \rightarrow R'_3SnR + MBr \qquad (1)$$

mechanistic aspects of this subtitution have received scrutiny,[2] and the general conclusions seem to be that for primary R groups, a predominantly direct (S_N2) displacement component (perhaps including some geminate process) is involved with $(CH_3)_3SnM$, but with secondary bromides, a configurationally unstable carbon-centered species is important. Triphenyltin alkalis, with secondary bromides,[1,3] exhibit predominantly stereochemical inversion at carbon whereas limited examination of the reactions of $(CH_3)_3GeLi$ with secondary bromides demonstrates substantial stereoleakage.[4] (Solvent and counterion effects of considerable importance can be superimposed in some systems.)[5] The reactions of certain alkylcyclohexyl bromides with $(CH_3)_3SnM$ provide product distributions consistent with the intervention of alkylcyclohexyl free radicals although other processes, e.g., carbanionic in nature, were not completely dismissed.[4,6] More recently,

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(1) Some of this work has been published in preliminary form: Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* 1981, *46*, 2423.

(2) Key references are contained in: Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* 1981, *103*, 833.

(3) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* 1971, *93*, 4047.

(4) Kitching, W.; Olszowy, H.; Waugh, J.; Doddrell, D. *J. Org. Chem.* 1978, *43*, 898.

(5) See, for example: Kuivila, H. G.; Considine, J. L.; Kennedy, J. D. *J. Am. Chem. Soc.* 1972, *94*, 7206.

(6) San Fillipo, J.; Silberman, J.; Fagan, P. J. *J. Am. Chem. Soc.* 1978, *100*, 4834.