135.3, 141.5, 142.7, 143.6, 145.7, 146.5, 153.6, 154.3.

Synthesis and Separation of 5(6)-Chloro-*N*-[(2,4-dinitrophenyl)thio]-2-methylbenzimidazole (4d). A solution of the arenesulfenyl chloride (1.230 g, 5.2 mmol) in dry THF was added dropwise to a stirred THF solution of 5-chloro-2-methylbenzimidazole (0.838 g, 5.0 mmol), and the mixture was allowed to stir for 4 h at room temperature. After filtration, the crude product, 1.797 g, was obtained by removal of solvent in vacuo. The first recrystallization from benzene and hexanes yielded 0.411 g (22.6%), mp 182–184.5 °C. The once-crystallized sulfenamide was again dissolved in a minimum of boiling benzene and filtered hot. To the hot benzene solution were added boiling hexanes until the solution became cloudy. The sulfenamide solution was allowed to cool slowly and then to sit at room temperature overnight. The pale yellow crystals were vacuum filtered and dried in a vacuum oven. High-field ^{1}H NMR indicated that one isomer is enriched 10:1: mp 188–189 °C; ^{1}H NMR (one isomer, $CDCl_3$) δ 2.64 (CH_3), 6.38 (d), 7.25–7.37 (m), 7.63 (d), 7.79 (s), 8.26 (q), 9.23 (d).

Registry No. **1a**, 1848-84-6; **1b**, 621-72-7; **1c**, 4857-04-9; **1d**, 91709-01-2; **2a**, 34569-15-8; **2b**, 7118-63-0; **2c**, 20443-38-3; **2d**, 2818-69-1; **3a**, 91709-02-3; **3b**, 91709-03-4; **3c**, 91709-04-5; **3d**, 91709-05-6; **4a**, 91709-06-7; **4b**, 91709-07-8; **4c** (5-chloro), 91709-08-9; **4c** (6-chloro), 95891-99-9; **4d** (5-chloro), 95864-47-4; **4d** (6-chloro), 95864-48-5; CH_3COOH, 64-19-7; $ClCH_2COOH$, 79-11-8; CH_3CH_2COOH, 79-09-4; $PhCH(CH_3)COOH$, 492-37-5; $PhCH_2COOH$, 103-82-2; *o*-phenylenediamine, 95-54-5; 4-chloro-*o*-phenylenediamine, 95-83-0; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7.

Kinetic Isotope Effects and Pressure Effects in Several Hydrogen-Transfer Reactions of Tetralin and Related Compounds

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The H/D kinetic isotope effects and activation volumes have been measured for several hydrogen-transfer reactions using tetralin, dihydronaphthalenes, cyclohexa-1,4-diene, and cyclohexanol as donors. The isotope effects were found to exhibit different patterns for reactions of different mechanisms. They indicate whether hydrogen is in transit in the activated complex and show the number of atoms in transit (one or two). The KIE for the reaction of tetralin with quinones is consistent with concerted transfer of two hydrogens whereas the other reactions were found to be stepwise. The activation volumes lie within the range −23 to −33 mL/mol and do not seem to differentiate among bimolecular mechanisms. The relevance to previous studies of the KIE and ΔV^* for coal hydrogenation reactions is discussed.

The mechanisms of reactions by which tetralin, dihydronaphthalenes, and cyclohexadienes transfer hydrogen to various reagents have been studied for more than 20 years, and yet there are many inconsistencies and puzzling results which remain to be clarified. Much of the work has been stimulated by the recent revival of interest in coal liquefaction which is often accomplished by indirect hydrogenation using tetralin or related donor solvents. Probably the most extensive survey of acceptors was conducted by Benjamin, Raaen, Maupin, Brown, and Collins,[1] who tested 53 potential acceptor compounds with tetralin as a donor. Dihydronaphthalenes, cyclohexadienes, and alcohols have also been used as reductive agents.[2-11] Free radical reactions, ionic reactions, and pericyclic reactions seem to be exemplified by one or another of the reagent combinations which have been studied to date.

Recently we have reported kinetic isotope effects for the reaction of subbituminous coal with several deuterated derivatives of tetralin and 1,2-dihydronaphthalene.[12] The pattern of effects was so different for these two hydrogen donors as to suggest that they react by different mechanisms. This result prompted us to test several model hydrogen-transfer reactions in order to determine whether the isotope effects can be reconciled with other evidence pertaining to mechanism.

A mechanistic path (Scheme I) which many have thought to be exhibited by the reaction of coal with tetralin is bond homolysis followed by hydrogen abstraction from a donor (DH_2).

Scheme I

$$R_2 \xrightarrow{\text{slow}} 2R\cdot$$

$$2R\cdot + DH_2 \xrightarrow{\text{fast}} 2RH + D$$

An example of this type which has been thoroughly studied is the conversion of bibenzyl to toluene. The measured activation energy and entropy are appropriate to the mechanism,[13,14] and even more revealing is the activation volume,[14] +31 mL/mol, which indicates bond

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breaking in the rate-controlling step. A reaction of this type should have no kinetic isotope effect. We have found no record of any previous investigation of this prediction.

Aside from homolysis, it is possible to generate radical intermediates by disproportionation as shown in Scheme II. Reactions thought to exhibit this mechanism are disproportionation of 1,2-dihydronaphthalene to naphthalene and tetralin[15] and cyclohexa-1,3-diene to benzene and cyclohexene.[16] This mechanism in contrast to the one above should have a negative activation volume, and it should also have a kinetic isotope effect. These effects have apparently not been investigated so far. The present evidence for the radical mechanism in the case of 1,2-dihydronaphthalene is very strong.[15] Use of deuterium tracers showed that the reaction is not stereospecific and therefore not concerted. The expected radical coupling products and solvent addition products were observed.

Scheme II

$$2RH_2 \xrightarrow{\text{slow}} RH\cdot + RH_3\cdot \xrightarrow{\text{fast}} R + RH_4$$

A third type of radical pathway applies to compounds having a three-atom bridge connecting aryl groups (Scheme III).

Scheme III

$$ArKLMHAr + R\cdot \xrightarrow{\text{initiation}} RH + ArKL\dot{M}Ar$$

$$ArKL\dot{M}Ar \rightarrow ArK\cdot + L{=}MAr$$

$$ArK\cdot + ArKLMHAr \rightarrow ArKH + ArKL\dot{M}Ar$$

Examples are 1,3-diphenylpropane, dibenzyl ether, and β-phenethyl phenyl ether.[17] Hydrogen donation will occur when a donor solvent is used,[18] but it is not an essential feature of the reaction. Compounds of this type are not included in the present study.

An ionic mechanism for transfer of hydrogen to an acceptor, A, can be formulated as shown in Scheme IV. The reaction of tetralin with quinones has long been thought to exemplify the hydride-transfer mechanism.[2] More recently it has been proposed for the reaction of 1,4-dihydronaphthalene, and 1,4-dihydrobenzene with quinones[4,19] and 1,2-dihydronaphthalene with tetracyanoethylene.[6] Oddly enough, the latter reaction is stereoselective, but the kinetic isotope effect indicates that it is not concerted.

Scheme IV

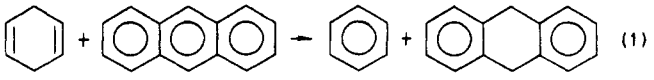
$$DH_2 + A \xrightarrow{\text{slow}} DH^+ + AH^- \xrightarrow{\text{fast}} D + AH_2$$

The most problematical mechanism to be proposed for hydrogen-transfer reactions is the symmetry-allowed pericyclic mechanism (Scheme V).

Scheme V

$$A + DH_2 \xrightarrow{\text{slow}} D + AH_2$$

A surprising number of such allowed reactions have failed mechanistic tests for concertedness. The reaction of cyclohexa-1,4-diene with anthracene as shown in eq 1



(1)

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is a symmetry-allowed 2 + 4 case cited by Woodwarrd and Hoffmann.[20] A study of this reaction by Fleming and Wildsmith[5] using deuterium as a tracer has shown that it is not stereospecific. The symmetry-allowed reactions of cyclohexa-1,3-diene were likewise found to be nonstereospecific. The reaction of 1,2-dihydronaphthalene with TCNE cited above is a closely related example of an allowed reaction which is not concerted, and hence not pericyclic, even though it is stereospecific. There is evidence, however, that the reactions of cyclohexa-1,4-dienes with quinones may be pericyclic. Stoos and Rocek[7] found that *cis*-3,6-dimethylcyclohexa-1,4-diene is more than 20 times as reactive as the trans isomer and that aromatizing dienes are 1000 times more reactive than analogues which do not aromatize. Virk[8-10] has proposed pericyclic mechanisms for the reaction of coal and model compounds with various hydrogen donors and has presented evidence based on reactivity and activation entropy. His examples of the reduction of polynuclear hydrocarbons by the dihydronaphthalenes have been challenged by King and Stock,[11] who showed that tetracene with a mixture of deuterated and undeuterated 1,4-dihydronaphthalene gave a significant amount of product containing one D atom.

In order to acquire additional evidence on the mechanisms of reaction of tetralin, the dihydronaphthalenes, and cyclohexanol as hydrogen donors, we have prepared deuterated derivatives designed to show by means of the kintic isotope effect (KIE) whether hydrogen in transit in the activated complex and, if so, whether the number of atoms is one or two. For a concerted transfer of two hydrogen atoms from tetralin (Scheme V) we would expect the compounds tetralin, tetralin-*1,1,4,4-d*$_4$, tetralin-*2,2,3,3-d*$_4$, and tetralin-d_{12} to have kinetic isotope effects in the proportions $1{:}X{:}X{:}X^2$ where X is the KIE for a single atom. Similarly for 1,2-dihydronaphthalene, 1,2-dihydronaphthalene-*1,1,3-d*$_3$, and 1,2-dihydronaphthalene-d_{10} we would expect the proportions $1{:}X{:}X^2$. For reaction by the homolysis controlled path (Scheme I) there should be no KIE. For reaction according to Scheme II with the donor as one of the components there should be a KIE for α-deuterated tetralin but not for β-deuterated (assuming significant α-selectivity). Likewise for 1,2-dihydronaphthalene there should be a KIE for the perdeuterated compound, but not for *1,1,3-d*$_3$ (assuming significant β-selectivity). For reaction by Scheme IV the pattern of KIE's should be the same as for Scheme II.

The activation volume could also be useful in some cases in discriminating mechanisms. In the case of the reaction of tetralin with thymoquinone[21] and bibenzyl[14] the difference is spectacular, −28 and +31 mL. This case involves a contrast of bimolecular and unimolecular mechanisms. Schemes II, IV, and V are all bimolecular, but certain differences could perhaps emerge. Pericyclic reactions are characterized by large negative activation volumes which are relatively insensitive to solvent.[17] The large magnitude is ascribed to the formation of two bonds. In Scheme II a single bond is involved and the magnitude out to be less. Scheme IV also involves a single bond but has the additional significant feature of ionic electrostriction. This usually causes the activation volume to be large and sensitive to solvent.

The long-range objective of this study is to identify a class of model compounds which resemble coal in their pattern of isotope effects and activation volumes in hy-

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Table I. Kinetic Isotope Effects for Reaction of Tetralin with Hydrogen Acceptors

acceptor	temp, °C	d_0	1,1,4,4-d_4	2,2,3,3-d_4	d_{12}
bibenzyl	400	(1.0)	1.0	1.0	1.0
thymoquinone	175	(1.0)	3.0	2.3	5.7
anthraquinone	295	(1.0)	1.8	1.8	3.2
indene	320–400	(1.0)	1.0	1.0	1.0
nitrosobenzene	215	(1.0)	1.7	1.1	1.7
2-nitroso-1-naphthol	240	(1.0)	1.6	nm	1.6
coal[a]	335	(1.0)	2.0	2.0	3.7

[a] Reference 12.

drogen-transfer reactions with tetralin and 1,2-dihydronaphthalene. A good match would imply similarity of mechanism, and the prospects for firmly establishing the mechanism are better for model compounds than for coal itself.

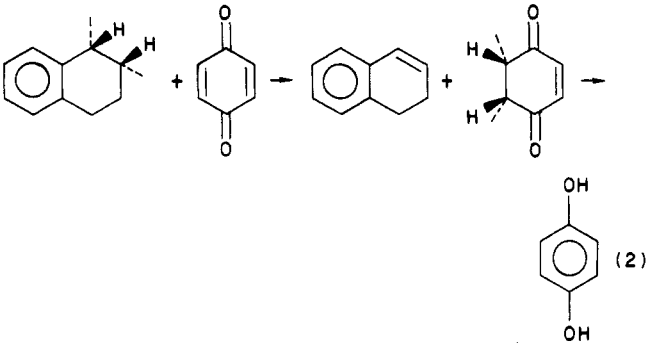
Results and Discussion

Reaction of Tetralin with Bibenzyl. We have found that the reaction rate is not affected by isotopic substitution at the α- or β-position of tetralin (Table I) in agreement with the prediction for rate-controlling homolysis followed by hydrogen abstraction.

Reaction of Tetralin with Quinones. The kinetic isotope effects for reaction of tetralin-d_0, -1,1,4,4-d_4, -2,2,3,3,-d_4, and -d_{12} with thymoquinone are 1:3.0:2.3:5.7 and with anthraquinone are 1:1.8:1.8:3.2, respectively (Table I). These results are consistent with those of Van der Jagt et al.,[23] who found that tetralin labeled with tritium at the 1-position reacts with 2,3-dichloro-5,6-dicyanobenzoquinone at 80 °C about 1.5 times slower than unlabeled tetralin. These authors, however, invoked a hydride-transfer mechanism to explain quinone hydrogenation. Our results, showing a substantial isotope effect for tetralin deuterated at the α-position, which is nearly equal to the effect for β-deuterated tetralin conform well to the pattern predicted for simultaneous transfer of two hydrogen atoms, thus strongly implying a pericyclic mechanism.

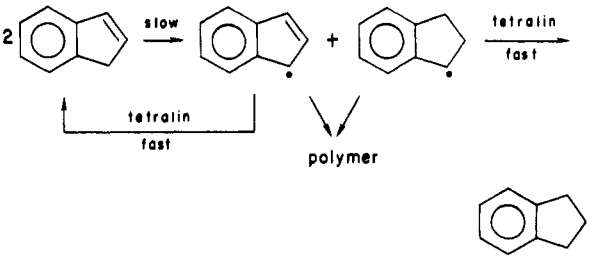
The fact that the KIE for perdeuterated tetralin exceeds the limit for the "ordinary" isotope effect in both cases (3.4 at 175 °C and 2.6 at 295 °C) could be explained by invoking the tunnel effect for a transfer of a single hydrogen, but in order to accommodate the effects observed for α- and β-deuterated compounds, one of two very implausible additional postulates would need to be fulfilled. It could be assumed that in the case of β-deuterated tetralin we observe a secondary isotope effect. This hypothesis is doubtful, since the secondary effect is usually much smaller. In one study involving free radicals, the secondary effect at β-carbon was 1.08/D atom.[24] Another way in which the results could be consistent with a stepwise mechanism is the possibility that the reaction is nonselective between the α- and β-position in tetralin. This postulate, however, is contradictory to all known facts about the reactivity of tetralin. For example, our method of synthesis of tetralin-1,1,4,4-d_4 and -2,2,3,3-d_4 was based on very strong selectivity of the α-position in ionic exchange under basic conditions. The abstraction of hydrogen from tetralin by photoexcited benzophenone at 78 °C gives only 1-tetralyl,[26] although there is evidence for a decline in selectivity at temperature above 430 °C.[27]

Thus, finally, it seems to be the most feasible explanation that the transfer of hydrogen atoms from tetralin to quinones is simultaneous. According to the Woodward–Hoffmann rules, this reaction will be symmetry allowed as supra–supra group transfer as shown in eq 2. The hydrogens are transferred to a carbon–carbon bond in the quinone ring, and hydroquinone is formed by rapid tautomerization.



(2)

Reaction of Tetralin with Indene. Significant conversion of indene to indane (99% at 400 °C) during reaction with excess tetralin was first reported by Benjamin et al.[1] This result is surprising because of the well-known tendency of indene to polymerize.[28] Later investigators reported much a lower yield of indane; at 360 °C after 30 min the yield of indane was 22.8% whereas the conversion of indene was 74.9%.[29] A large amount of polymeric material was observed during our attempts to investigate the influence of isotopic substitution on the reaction rate. The absence of any isotope effect for perdeuterated as well as for α- and β-deuterated tetralin (Table I) indicates that the transfer of hydrogen from tetralin is not involved in the rate-controlling step of the reaction. These findings and the susceptibility to polymerization suggest strongly that formation of relatively stable radicals is the slow step of the reaction. Molecular disproportionation seems to be the only plausible pathway of generation of radicals from indene. Therefore we propose the mechanism shown in eq 3 for the reaction between indene and tetralin. Indenyl



(3)

and indanyl radicals should be stabilized by delocalization of the odd electron. The pressure effect studies on hydrogenation of indene with tetralin are consistent with molecular disproportionation, since the reaction is accelerated by pressure.

Reaction of Tetralin with Nitroso Compounds. The kinetic isotope effects for reaction of nitrosocompounds with tetralin are presented in Table I. These results conform well to the pattern predicted for stepwise loss of

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Table II. Kinetic Isotope Effects for Reaction of 1,2-Dihydronaphthalene with Hydrogen Acceptors

acceptor	temp, °C	d_0	1,1,3-d_3	d_{10}
1,2-dihydronaphthalene	290	(1.0)	1.01	2.3
thymoquinone	140	(1.0)	1.07	4.0
dimethyl maleate	220	(1.0)	1.01	2.1
coal[a]	220	(1.0)	1.1	2.7

[a] Reference 12.

hydrogen starting at the α-position in tetralin. The isotope effect, 1.1, found for the reaction of nitrosobenzene with β-deuterated tetralin appears to be a secondary effect. The reaction intermediate can be either a radical or a cation, since the KIE pattern is the same in both cases. We have not found in the literature any information on the reaction of tetralin with nitrosocompounds, but further studies to clarify the details of the mechanism lie beyond the scope of this work. We measured the reaction rates for deuterium-substituted tetralins in order to reassure ouselves that the KIE is appropriate to stepwise loss of hydrogen from tetralin rather than to explain the details of the particular process.

Disproportionation of 1,2-Dihydronaphthalene. It has been found that 1,2-dihydronaphthalene at 300 °C undergoes decomposition to naphthalene and tetralin by the transfer of hydrogen from one molecule to another.[11,15,30] Gill and associates[30] established second-order kinetics and reported little change of rate constant with the variation of solvent or with addition of radical inhibitors, although the reaction was accelerated by addition of radical initiators. Heesing and Mullers[15] found that the reaction is not stereospecific by studying decomposition of *cis*- and *trans*-1,2-dihydronaphthalene-*1,2*-d_2. The combined evidence strongly implies reaction by Scheme II in which the rate-determining step is transfer of a single hydrogen atom to produce tetralyl radical and hydronaphthyl radical. Further reaction gives tetralin and naphthalene. We include this reaction in the present study in order to test whether the KIE will behave as expected for the stepwise hydrogen-transfer mechanism. As shown in Table II the KIE for the perdeuterio compound is 2.3, which is appropriate for the transfer of a single hydrogen atom at 290 °C (the classical limit, based on IR frequencies, is 2.6 at that temperature). The very small effect found for 1,2-dihydronaphthalene-*1,1,3*-d_0 appears to be secondary and indicates that hydrogen is transferred from the 2-position in the rate-determining step as previously proposed.[15]

It may be also noteworthy that the rate constant of 1.95×10^{-5} L/(mol s) we found for decomposition of 1,2-dihydronaphthalene without any solvent is in good agreement with kinetic data reported by Gill.[30]

Reaction of 1,2-Dihydronaphthalene with Thymoquinone and Dimethyl Maleate. For the reaction of 1,2-dihydronaphthalene with thymoquinone and dimethyl maleate the same pattern of kinetic isotope effect was found (Table II). These results agree well with those of Heesing and Mullers[6] for the reaction with tetracyanoethylene. They found 1.1 for *1,1*-d_2 and 2.8 for the *2,2*-d_2 deuterated donor. It is apparent that in the rate-controlling step a single hydrogen is being transferred from the 2-position. Both sets of results show that the secondary isotope effect is small and in the expected range.

Reaction of 1,4-Dihydronaphthalene with Anthracene. The Woodward–Hoffmann rules allow a pericyclic reaction with 1,4-DHN but not with the 1,2-isomer. Virk and associates found a 10-fold higher reactivity for 1,4-DHN and concluded that the reaction is pericyclic.

The relative instability and high reactivity of 1,4-dihydronaphthalene compared to 1,2-dihydronaphthalene have long been known (the heats of formation of 1,2- and 1,4-dihydronaphthalene in the liquid phase are 18 and 21 kcal/mol, respectively)[31] and could account for the preference of 1,4- over 1,2-dihydronaphthalene as reductive agent regardless of orbital symmetry. Nevertheless, the possible involvement of a pericyclic mechanism should not be summarily ruled out. If a very high value of the kinetic isotope effect were found, the proposition would be vindicated. As it happens, however, the measured value of 2.9 at 220 °C lies well within the theoretical limits for the transfer of a single hydrogen and does not support the pericyclic mechanism.

Reaction of Cyclohexanol with Anthracene. Another group of reactions postulated by Virk[10] to be pericyclic was that of secondary alcohols and certain aromatic hydrocarbons. The reaction of cyclohexanol with anthracene was supposed to exemplify favorable supra–supra stereochemistry whereas the reaction of cyclohexanol with phenanthrene has much less favorable supra–antara stereochemistry. Both hydrogen transfers were bimolecular.

In order to acquire additional evidence on the mechanism of these reactions, we attempted to measure isotope effects. We failed to achieve measurable hydrogen transfer from cyclohexanol to phenanthrene, but anthracene was hydrogenated to 9,10-dihydro compound with a second-order rate constant of 1.1×10^{-6} L/(mol s) at 350 °C, in good agreement with the previous report.[10] The KIE was 3.5 for perdeuteriocyclohexanol and 1.3 for $C_6H_{11}OD$. This result is inconsistent with the hypothesis that hydrogen atoms bonded to oxygen and carbon are transferred simultaneously. The value of the KIE for OH bond rupture is too small for this breakage be a part of the rate-determining step. The studies of KIE involved in oxidations of alcohols by bromine in aqueous solutions show a similar isotope effect. Kaplan[32] found that the reaction of bromine with CH_3CD_2OH proceeds 4.3 times slower than the reaction with ethanol, which shows that the slow step involves the rupture of a carbon–hydrogen bond. For a similar reaction Swain et al.[25] observed a KIE of 2.9 when deuterium was substituted for hydrogen in the C–H bond of 2-propanol and 1.5 for substitution in the OH group. The latter results were explained on the basis that a hydride ion is transferred from carbon in the rate-controlling step and is followed by fast transfer of proton from oxygen. In summary, all the KIE confirm a stepwise mode of reaction, presumably with an ion as intermediate. This is not surprising, since the energy required for dissociation of the C–H bond is probably about 25 kcal/mol lower than for the O–H bond. For example, the bond dissociation energy for H–OH is 119 kcal/mol whereas for H–CH_2OH it is 93 kcal/mol.[33] Our observation of a strong isotope effect for perdeuterated alcohol slightly exceeding the theoretical limit suggests involvement of tunneling in the hydrogen-transfer process.

Activation Volumes. The results of activation volume measurements are presented in Table III. All the values obtained lie within the narrow range −23 to −33 mL/mol.

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Table III. Activation Volumes for Several Hydrogen Transfer Reactions

donor	acceptor	temp, °C	mL/mol
1,2-dihydro-naphthalene	1,2-dihydronaphthalene	260	−25
1,2-dihydro-naphthalene	dimethyl maleate	220	−29
1,4-dihydro-naphthalene	anthracene	220	−23
1,4-cyclohexadiene	anthracene	200	−31
1,4-cyclohexadiene	thymoquinone	75	−33
tetralin	thymoquinone	175	−28[a]
tetralin	coal	344	−27[a]

[a] Reference 21.

The activation volume for disproportionation of 1,2-dihydronaphthalene, −25 mL/mol, is more negative than for most bimolecular reactions leading to formation of a single bond without electrostriction (see ref 22 for a survey), but the tendency of high temperatures to magnify activation volumes is probably an important factor.[14] The activation volumes for other hydrogen transfers from dihydronaphthalenes and cyclohexa-1,4-diene have similar values. As established by kinetic isotope effects studies, the rate-determining step of all these reactions involves transfer of a single hydrogen either as an atom or as hydride ion. This is a bit disconcerting, since for the ionic mechanism one might justifiably predict an activation volume of about −50 mL/mol by analogy to the displacement reaction of piperidine with aryl halides[34] at temperatures near 200 °C. A negative activation volume of −15 mL/mol has been found for the Cannizzaro reaction of benzaldehyde,[35] which is thought to be a hydride-transfer reaction without change of electrostriction.

The activation volume for the reaction of tetralin with thymoquinone is −28 mL/mol.[21] The isotope effects make it seem almost certain that this reaction proceeds by different mechanism than reactions with 1,2-dihydronaphthalenes, yet activation volumes are equal within experimental error. This could be due to compensation if one assumes that the former is a two-bond reaction without electrostriction whereas the latter involves the formation of one bond with electrostriction. If it were possible to use solvents with a wide range of polarity, it might be possible to diagnose the electrostrictive contribution, but we have found no polar solvents which are inert under the reaction conditions.

Pertinence to Coal. The results of the KIE and $\Delta V^{\ddagger}$ for the model compounds described above show that quinones most nearly resemble coal with regard to hydrogenation by tetralin and 1,2-dihydronaphthalene. The previously reported KIE for the reaction of coal with tetralin-*1,1,4,4-d*$_4$, -*2,2,3,3-d*$_4$, and -d_{12} was 2.2:2.2:3.7.[12] Both thymoquinone and anthraquinone exhibit a similar pattern. All other acceptors (anthracene, phenanthrene, dimethyl maleate, bibenzyl, indene, cyclohexene, nitroso compounds) showed different patterns of KIE.

The isotope effects for the reaction of quinones with 1,2-dihydronaphthalene were also similar to those for coal. However, our attempts to study the reactions of coal with 1,4-dihydronaphthalene and cyclohexa-1,4-diene have failed because of significant disproportionation of these solvents. The disproportionation was not observed in the presence of thymoquinone, but the reaction temperatures were much lower in the latter case.

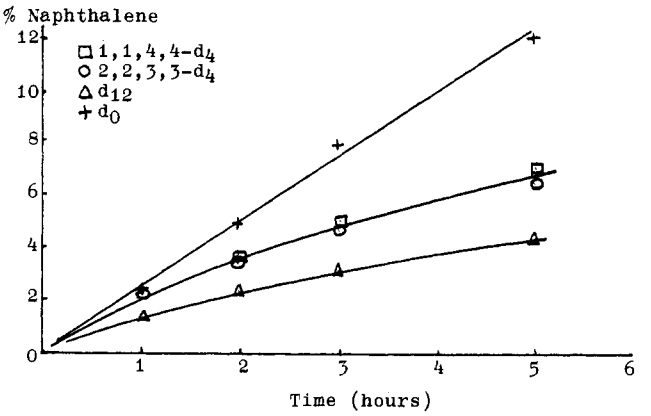

Figure 1. Reaction of anthraquinone with tetralin.

Although quinonoid features are not believed to be a major part of coal structure, they may be produced by enol–keto tautomerization. Such tautomerism was invoked to explain conversion of (hydroxyphenyl)phenylmethanes to phenol and toluene in tetralin.[13] There is also a possibility that other structures present in coal, which we have not studied, react with tetralin in the same way.

The studies involving cyclohexanol suggest that the reaction of coal with alcohols may be ionic even in the absence of added base.

Experimental Section

Materials. The procedures to obtain tetralin-*1,1,4,4-d*$_4$, -*2,2,3,3-d*$_4$, and -d_{12} and 1,2-dihydronaphthalene-*1,1,3-d*$_3$ and -d_{10} were described previously.[12]

1,4-Dihydronaphthalene was obtained by Birch reduction of naphthalene. A solution of 10 g of naphthalene in 200 mL of anhydrous ethanol was placed in a 500-mL flask equipped with a reflux condenser and a magnetic stirrer. Sodium metal (16 g) was added in small pieces over a period of 1.5 h. The reaction mixture was neutralized with 40 mL of acetic acid in order to prevent rearrangement of 1,4-dihydronaphthalene into 1,2-dihydronaphthalene, and most of the ethanol was then removed by distillation under reduced pressure. The residue was partitioned between water and hexane, and the organic layer was dried and distilled to give 6.5 g of product, bp 204–205 °C (650 mmHg). Analysis by GC indicated 9% admixture of 1,2-dihydronaphthalene.

1,4-Dihydronaphthalene-d_{10} was obtained in the similar way except that naphthalene-d_8, EtOD, and CH_3COOD were used rather than naphthalene, EtOH, and CH_3COOH. The final product contained 93% of deuterium as indicated by NMR and density measurements.

Thymoquinone was prepared according to the procedure of Kermers, Wakeman, and Hixon.[36]

Nitrosobenzene was synthesized by the procedure of Coleman, McCloskey, and Stuart.[37]

Cyclohexanol-d_1 was obtained by exchange of deuterium between cyclohexanol and D_2O. Shaking a mixture containing a large excess of D_2O resulted in 98% replacement of H by D as indicated by NMR.

Other reactants used in this study were obtained commercially.

KIE Measurements. The reaction mixtures were prepared by placing appropriate components into glass tubes and sealing them. One reaction mixture contained protium donor and the other contained deuterated derivatives. After being heated for a selected time and temperature, the reaction mixtures were analyzed by a Tracor 565 capillary GC.

Reaction of Bibenzyl with Tetralin. A mixture containing bibenzyl and tetralin (molar ratio 1:7) was maintained at 400 °C

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(35) Brower, K. R.; Hughes, D. *J. Am.* Chem. *Soc.* **1978**, *100*, 7591.
(36) Kermers, E.; Wakeman, N.; Hixon, R. M. "Organic Syntheses"; Wiley: New York, 1941; Coll. Vol. 1, p 511.
(37) Coleman, G. H.; McCloskey, Ch. M.; Stuart, F. M. "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. III, p 668.

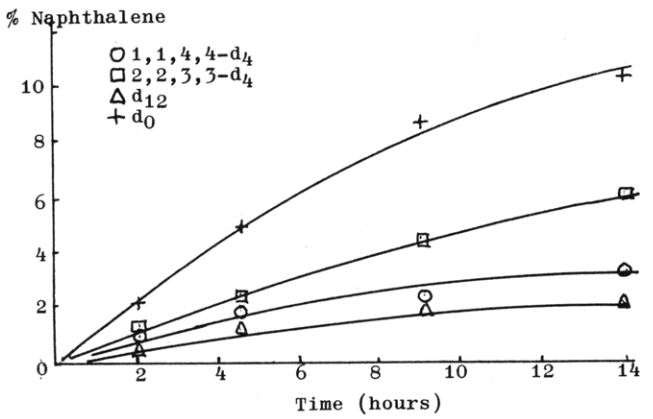

Figure 2. Reaction of thymoquinone with tetralin.

Table IV. Relative Times for a Fixed Conversion of Deuterated Tetralins in the Reaction with Anthraquinone

% naphthalene	d_0	d_{12}	*1,1,4,4-d_4*	*2,2,3,3-d_4*
3	(1.0)	2.7	1.6	1.6
4	(1.0)	2.9	1.7	1.7
5	(1.0)	3.3	1.9	1.8
6	(1.0)	3.0	2.0	1.9

Table V. Weight Percent of Indene in C_9 Fraction

temp, °C	time, min	d_0	d_{12}	*1,1,4,4-d_4*	*2,2,3,3-d_4*
320	150	47	47	48	47
340	75	66	67	65	68
400	15	60	62	51	63

Table VI. Relative Times for a Fixed Conversion of Deuterated Tetralins in the Reaction with 2-Nitroso-1-naphthol

% naphthalene	d_0	d_{12}	*1,1,4,4-d_4*
10	(1.0)	1.5	1.5
15	(1.0)	1.4	1.4
20	(1.0)	1.4	1.4

over a period of 9 h. Tetralin-d_0, tetralin-*1,1,4,4-d_4*, and -d_{10} were used as donors, and for each of them the degree of conversion to toluene was 40%.

Reaction of Tetralin with Quinones. For anthraquinone the starting mixtures were composed of 2 mol of tetralin/mol of quinone and the temperature was 295 C. The course of formation of naphthalene was followed by GC and is shown in Figure 1. Since the relatives times required for conversion to a given percentage of naphthalene are the reciprocals of the relatives rates, they are equal to the kinetic isotope effects expressed as $rate_H/rate_D$. Table IV presents the results derived from Figure 1. Corrected for isotopic purity, the KIE for tetralin-*1,1,4,4-d_4*, -*2,2,3,3-d_4*, and -d_{12} are 1.8, 1.8, and 3.2. For thymoquinone the starting mixtures were composed of 1:2.5 quinone/tetralin molar ratio, and the reaction temperature was 175 °C. Weight percentages of naphthalene obtained by GC analysis were plotted against time for each deuterium derivative of tetralin (Figure 2), and the relative reaction times were determined in the same way as for anthraquinone. The KIE values are shown in Table I.

Reaction of Indene with Tetralin. The reaction mixtures contained indene and tetralin in 1:10 molar ratio. The hydrogenation of indene to indane was followed by measuring the weight percentage of indane in the C_9 fraction. Only a part of the starting C_9 material appeared in the gas chromatogram because of loss due largely to polymerization. Reaction conditions and results are presented in Table V.

Reaction of Nitrosoarenes with Tetralin. For 2-nitroso-1-naphthol the reaction temperature was 240 °C, and the starting mixture contained equimolar amounts of donor and acceptor. The course of naphthalene formation is shown in Figure 3. After deriving the relative reaction times for deuterated tetralins (Table VI) and correcting for isotopic purity, we calculated KIE as 1.6 for both tetralins (see Table I). For nitrosobenzene the most convenient temperature for KIE measurement was 215 °C. All other conditions were the same as for 2-nitroso-1-naphthol. The calculated KIE are presented in Table I.

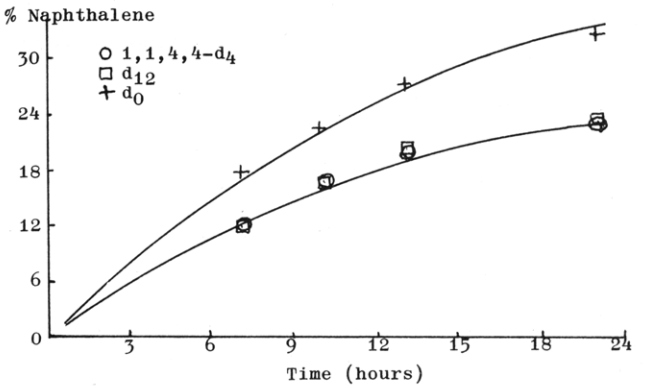

Figure 3. Reaction of 2-nitroso-1-naphthol with tetralin.

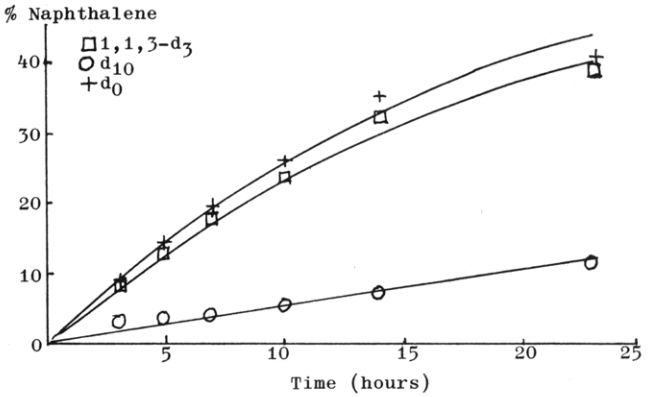

Figure 4. Reaction of 1,2-dihydronaphthalene with thymoquinone.

Table VII. Rate Data for the Disproportionation of 1,2-Dihydronaphthalenes

1,2-DHN	time, h	% naphthalene	10^5k, L/(mol s)
d_0	1	17.3	1.91
d_0	4	34.3	1.98
d_{10}	1	10.0	0.91
d_{10}	4	25.3	0.93
1,1,3-d_3	1	17.5	1.95
1,1,3-d_3	4	34.6	2.04

Disproportionation of 1,2-Dihydronaphthalene. Since the reaction is known to obey a second-order rate law,[30] the KIE were calculated from the rate constants. Reaction rates were measured at 290 °C, and no solvent was used. The conversion of 1,2-dihydronaphthalene to naphthalene and the calculated rate constants are shown in Table VII. Table II contains average values after correction for isotopic purity.

Reaction of 1,2-Dihydronaphthalene with Thymoquinone. The reaction conditions and procedure were similar to those used for the reaction with tetralin except for the temperature, which was 140 °C. Figure 4 presents the course of naphthalene formation. Applying the usual calculation method, we found the KIE values shown in Table II.

Reaction of 1,2-Dihydronaphthalene with Dimethyl Maleate. The reaction was carried out at 220 °C under first-order conditions. The molar ratio of 1,2-dihydronaphthalene to dimethyl maleate was 10:1. The conversion of dimethyl maleate to dimethyl succinate was followed by GC, and the pseudo first-order rate constant was calculated from the formula, $\exp(kt) = 100/(100 - Y)$, where Y is the weight percent of dimethyl succinate in dimethyl maleate–dimethyl succinate mixture. The following rate constants were obtained: 6.15×10^{-6} s^{-1} for 1,2-dihydronaphthalene, 6.11×10^{-6} s^{-1} for dihydronaphthalene-*1,1,3-d_3*, and

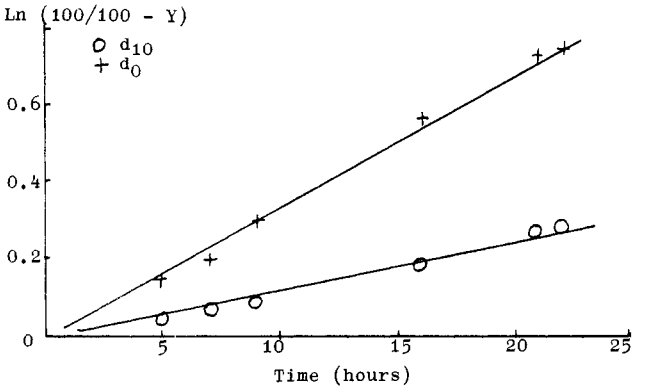

Figure 5. Reaction of 1,4-dihydronaphthalene with anthracene.

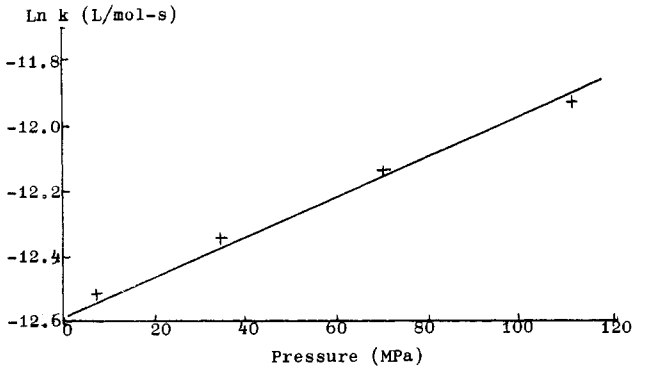

Figure 6. Pressure effect on disproportionation of 1,2-dihydronaphthalene.

3.35×10^{-6} s^{-1} for the d_{10} compound. Comparison of the rate constants and correction for isotopic purity gave KIE values presented in Table II.

Reaction of 1,4-Dihydronaphthalene with Anthracene. This reaction was also carried out under pseudo-first-order conditions. The molar ratio of 1,4-dihydronaphthalene to anthracene was 7:1. The reaction temperature was 220 °C. The conversion of anthracene to 9,10-dihydroanthracene was followed by GC, and the pseudo first-order rate constants were evaluated as described above (Figure 5). After correction for isotopic purity, we found KIE = 2.9 for perdeuterio-1,4-dihydronaphthalene.

Reaction of Anthracene with Cyclohexanol. The reaction rates were measured for the protium compound, $C_6H_{11}OD$, and cyclohexanol-d_{12}. The molar ratio of cyclohexanol to anthracene was 5:1, and the reaction temperature was 350 °C. The conversion of anthracene to 9,10-dihydroanthracene was followed by GC. The average second-order rate constants were 11×10^{-7} L/(mol s), 8.5×10^{-7} L/(mol s), and 3.2×10^{-7} L/(mol s) for $C_6H_{11}OH$, $C_6H_{11}OD$, and $C_6D_{11}OD$, respectively. Products of deuterium exchange (deuterated anthracene, H-containing perdeuteriocyclohexanol) were detected by GC/MS (a Hewlett-Packard 5790 MS detector with 5890A capillary GC) studies. GC/MS (a Hewlett-Packard 5790 MS detector with 5890A capillary GC) studies.

Table VIII. Rate Data for Activation Volume Measurements

Disporportionation of 1,2-Dihydronaphthalene				
P, MPa	6.9	34.5	69.0	110.3
10^6K, L/(mol s)	3.58	4.26	5.35	6.47
Dimethyl Maleate and 1,2-Dihydronaphthalene				
P, MPa	34.5	69.0	103.4	
10^6K, s^{-1}	8.1	10.1	13.2	
Anthracene and 1,4-Dihydronaphthalene				
P, MPa	34.5	69.0	103.4	
10^6k, s^{-1}	10.3	12.9	15.4	
Anthracene and 1,4-Cyclohexadiene				
P, MPa	34.5	69.0	103.4	
10^6K, s^{-1}	8.6	11.7	14.9	
Thymoquinone and 1,4-Cyclohexadiene				
P, MPa	6.9	34.5	69.7	
10^5k, s^{-1}	2.5	3.8	5.6	

Activation Volume Measurements. Glass syringes with the metal tip removed and the bottom converted to a test tube end were used as the reaction cells. After a reaction mixture was placed into the barrel, the plunger was inserted under reduced pressure. The cell was inserted into a high-pressure reactor, which was then filled with pressurizing fluid and placed in the thermostat (the high-pressure equipment and heating device have been previously described[14]). The pressure in the system was controlled by pumping or releasing the fluid as required. After the selected reaction time, the reactor was cooled and reaction mixture removed from the cell and analyzed by GC. The activaton volumes, ΔV^*, were obtained from plots of ln k vs. P according to the equation: $\Delta V^* = -RT(\partial \ln k/\partial P)_T$. Figure 6 presents such a plot for the disproportionation of 1,2-dihydronaphthalene. The reaction temperatures and final vlaues of ΔV^* are presented in Table III. The rate data are presented in Table VIII. Except for disproportionation of 1,2-dihydronaphthalene, all reactions were carried out under pseudo-first-order conditions. The fraction of hydrogenated product was followed by GC (with exception of the reaction of cyclohexa-1,4-diene with thymoquinone, where formation of benzene was measured).

Error. On the basis of repeatability we estimate that the relative error involved in reported values of KIE and ΔV^* is ±10%. There was no noteworthy variation in repeatability from one reaction to another.

Registry No. Tetralin, 119-64-2; 1,2-dihydronaphthalene, 447-53-0; bibenzyl, 103-29-7; thymoquinone, 490-91-5; anthraquinone, 84-65-1; indene, 95-13-6; nitrosobenzene, 586-96-9; 2-nitroso-1-naphthol, 132-53-6; dimethyl maleate, 624-48-6; anthracene, 120-12-7; 1,4-cyclohexadiene, 628-41-1; deuterium, 7782-39-0; cyclohexanol, 108-93-0.

Synthesis and Interconversion of Oxepanes and Bicyclo[3.2.1]octanes

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Methods for the synthesis of 2,2-dialkyl-substituted oxepanes (**3a–d**) and the corresponding 4,4-dialkyldioxabicyclo[3.2.1]octanes (**4a–d**) are described. The interconversion of the oxepane and dioxabicyclo[3.2.1]octane systems, particularly through the methoxyimino derivatives, is discussed. The use of each of the above oxepanes and bicyclic analogues as substrates for Wittig reactions to generate zoapatanol analogues is also described.

Recent papers from these laboratories have described the isolation, structure proof, and total synthesis of the novel oxepane diterpenoid zoapatanol (**1**) and the total synthesis of its dioxabicyclo[3.2.1]octane analogue **2**.[1,2]

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