

Chapter 3

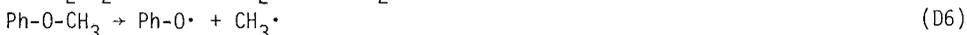
THERMAL REACTIONS OF COAL

This chapter deals with the rate parameters of the principal elementary reactions of pyrolysis, hydrolysis and liquid-phase hydrogenation. While considerable data is available in the literature about rate parameters, in most cases recourse must be made to estimation techniques such as group additivity and transition state theory. These two techniques, group additivity in particular, have been largely developed by Benson and coworkers (e.g. refs. 29,30) and are popularly known as thermochemical kinetics. Much of this chapter is taken up by the application of thermochemical kinetics to various elementary reactions of interest. The estimated parameters along with those taken from the literature are compiled in a table at the end of the chapter.

One of the uncertainties associated with estimating rate parameters for coal reactions is due to the condensed nature of the coal phase which is the reaction medium. Almost all reported rate values and group contribution information refer to gas phase kinetics. Another uncertainty arises from the fact that coal molecules contain, primarily, condensed ring aromatics while much of the reported experimental information refers to single ring compounds. When these uncertainties are added to the significant uncertainty associated with the structure of the transition state and the frequencies of its vibrational modes it will be realized that estimated A-factors could be easily in error by a factor of ten. Nevertheless, the estimates discussed here are very useful in the absence of other information and can obviously be improved by comparison with data from model compound studies. With these difficulties in mind we now proceed to examine several classes of reactions: bond dissociation, hydrogen abstraction and hydrogen addition. These are all free radical reactions. Reactions other than free radical, e.g. concerted reactions, have only recently been examined relative to coal pyrolysis and will be briefly surveyed in the last section.

3.1 BOND DISSOCIATION WITH PRODUCTION OF TWO RADICALS

The following reactions will be considered with Ph, Ph' representing aromatic nuclei such as naphthalene, phenanthrene, etc.





The rate of each of these elementary reactions can be expressed in the Arrhenius form

$$k = A \exp(-E/RT)$$

where A is the "A-factor" and E the experimental activation energy, both being functions of temperature. The activation energy E can be estimated using the fact that the reverse reaction, free radical recombination, has very small activation energy which is conventionally taken as zero. Thus

$$E = \Delta H \quad (3.1)$$

where ΔH is the standard heat (or enthalpy) of reaction, at the temperature of interest and pressure of one atmosphere. ΔH is also somewhat less accurately known as the bond dissociation "energy". The heat of reaction ΔH can be estimated by the group additivity method as shown in the examples below.

The A-factor is given by transition state theory as

$$A = e \frac{k_B T}{h} \exp(\Delta S^{\ddagger}/R) \quad (3.2)$$

where ΔS^{\ddagger} is the standard (atmospheric pressure) activation entropy, i.e. the difference in entropy between the transition state (or activated complex) and the reactants. The activation entropy can be estimated by the methods of statistical mechanics if the structure of the activated complex is known. This estimation involves a great deal of uncertainty because of lack of reliable information about several of the vibrational frequencies of the activated complex.

Benson and O'Neal (ref. 29) have evaluated experimental data for several of the reactions (D1)-(D8) and have recommended preferred parameter values in each case. In the following subsections we shall illustrate the theoretical estimation techniques on reactions which are not included in the compendium of Benson and O'Neal. The estimated parameters along with values from the literature are listed in the table at the end of the chapter.

Examples 1 to 5 treat the estimation of activation energies while examples 6 to 8 the estimation of A-factors.

3.1.1 Activation energies

Example 1.

In this example we examine reaction D1 with Ph an unsubstituted phenyl. The calculations will be initially made for 300°K since most of the available data refer to that temperature. Subsequently, the estimate will be revised to apply to 800°K. The heat of reaction can be expressed in terms of heats of formation as $\Delta H = \Delta_f H(\text{H}\cdot) + \Delta_f H(\text{Ph-CH}_2\cdot) - \Delta_f H(\text{Ph-CH}_3)$

The last two terms can be estimated by group additivity as follows:

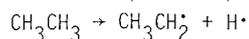
$$\Delta_f H(\text{Ph-CH}_2\cdot) = 5[C_B-(\text{H})] + [C_B-(\text{C}\cdot)] + [C\cdot-(C_B)(\text{H})_2]$$

$$\Delta_f H(\text{Ph-CH}_3) = 5[C_B-(\text{H})] + [C_B-(\text{C})] + [C-(C_B)(\text{H})_3]$$

where the brackets denote heats of formation and the groups within the brackets are written with the notation of ref. 30. The tables in ref. 30 give $[C_B-(\text{C}\cdot)] = [C_B-(\text{C})]$, hence

$$\Delta H = [H\cdot] + [C\cdot-(C_B)(\text{H})_2] - [C-(C_B)(\text{H})_3] = 52.1 + 23.0 - (-10.2) = 85.3 \text{ kcal/g-mol.}$$

For comparison purposes we examine the aliphatic analog,



for which

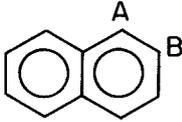
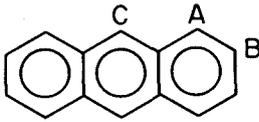
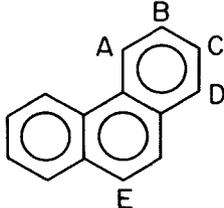
$$\Delta H = [H\cdot] + [C\cdot-(\text{C})(\text{H})_2] - [C-(\text{C})(\text{H})_3] = 98.1$$

The difference between the two energies

$$[C\cdot-(\text{C})(\text{H})_2] - [C\cdot-(C_B)(\text{H})_2] = 12.8 \text{ kcal/g-mol}$$

is due to the interaction of the free electron with the π -bonding orbital of the benzene ring and is called the resonance stabilization energy (RSE). The RSE is responsible for the relatively low value of several bond dissociation energies in coal. Table 3.1 lists the RSE of α -radicals deriving from larger rings as estimated by Stein et al. (ref. 31).

TABLE 3.1 Resonance stabilization energies (kcal/g-mol) for radical with $\text{CH}_2\cdot$ at position A,B,C,D,E (ref. 31).

| Compound | A | B | C | D | E |
|---|------|------|------|------|------|
|  | 13.0 | | | | |
|  | 16.4 | 14.7 | | | |
|  | 18.5 | 15.3 | 22.2 | | |
|  | 15.0 | 15.0 | 14.0 | 16.0 | 16.0 |

Using the RSE values of Table 3.1 we can estimate the heat of various dissociation reactions as shown in the following examples. For convenience we shall use the notation Ph_1 = phenyl, Ph_2 = naphthyl, Ph_3 = phenanthryl. Furthermore, Ph_2^2 will denote 2-naphthyl, Ph_3^1 will denote 1-phenanthryl, etc.

Example 3.2

We consider the reaction



and its aliphatic analog



The heat of (D2a) is well established (ref. 30) as 85, hence using the RSE value of 14.9, we estimate for reaction (D2'), $\Delta H = 85 - 14.9 = 70.1$.

Example 3.3

To estimate the heat of reaction



we start from the simpler



for which ΔH can be computed by group additivity using the values of ref. 30:

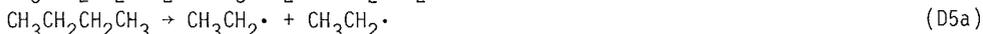
$$\Delta H(\text{D4}'') = [\text{Ph}_1\text{-CH}_2\cdot] + [\text{Ph}_1\cdot] - 10[\text{C}_B\text{-(C}_B)] - 2[\text{C}_B\text{-(C)}] - [\text{C-(C}_B)_2] = 45 + 78.5 - 10 \times 3.3 - 2 \times 5.51 - (-4.86) = 84.3.$$

The difference between the heats of reactions (D4') and (D4'') is equal to the difference of the corresponding RSE which is 3.6, therefore $\Delta H(\text{D4}') = 84.3 - 3.6 = 80.7$.

Because of this large value of ΔH , the rate of direct dissociation of methylene bridges is negligible relative to other pyrolysis reactions. However, two indirect dissociation mechanisms are much more energetically favorable. The first proceeds by the addition of hydrogen atoms and other small radicals to the aromatic ring. The second is operative in the presence of phenolic hydroxyl groups in the ortho and para position. These two mechanisms will be discussed in following subsections.

Example 3.4

Here we consider reaction (D5) and its aliphatic analog,



The heat of (D5a) is 82, so that using the appropriate RSE values from Table 3.1 we obtain $\Delta H(\text{D5}') = 82 - 15.6 - 16.6 = 49.8$.

Example 3.5

We next estimate the heats of reactions (D6)-(D8) which involve the dissociation of carbon-oxygen bonds. Because the heats of formation of the phenoxy radicals ($\text{Ph-O}\cdot$) are not available we will assume that their resonance stabilization energies are the same as those of the corresponding benzyl radicals,

$$[\text{O}\cdot\text{-(C)}] - [\text{O}\cdot\text{-(C}_B)] = [\text{C}\cdot\text{-(C)(H)}_2] - [\text{C}\cdot\text{-(C}_B)(\text{H)}_2] = 12.8$$

The value of $[O\cdot-(C)]$ can be calculated from the heat of formation of $CH_3CH_2O\cdot$, $\Delta_f H[CH_3CH_2O\cdot] = [O\cdot-(C)] + [C-(C)(H)_2(O\cdot)] + [C-(C)(H)_3]$. In this equation $\Delta_f H[CH_3CH_2O\cdot]$, $[C-(C)(H)_3]$ are listed in reference 30, while $[C-(C)(H)_2(O\cdot)]$ may be approximated by $[C-(C)(H)_2(O)]$. The result is $[O\cdot-(C)] = 14.3$ so that $[O\cdot-(C_B)] = 14.3 - 12.8 = 1.5$. Using this value in group additivity calculations we find the heats of reactions (D6),(D7),(D8) to be 68.3, 85.5, 55.6 which vary by no more than ± 3 kcal from the heats of reactions (D2),(D3), and (D4), respectively.

Since the aromatic nuclei in coal are substituted to a considerable degree we must consider the effect of substituents on the heats of the bond dissociation reactions. Barton and Stein (ref. 32) conducted some model compound studies showing that the heat of reaction (D2) is reduced by about 1 to 2 kcal/g-mol by an ortho-methyl substituent. Meta and para substituents were found to have little or no effect. Earlier studies summarized in reference 32 had shown that meta substitution by a methyl group has no effect, para has a slight effect and ortho has a more significant effect, up to 3 kcal/g-mol. An investigation of the pyrolysis of cresols (ref. 33) showed that o-cresol reacts faster than m-cresol by a factor of about three at 806°K. In both cases the rate determining step was the dissociation of a benzylic hydrogen. Assuming equal A-factors, the activation energy in the ortho-compound must be lower than that of the meta-compound by about 2 kcal/g-mol.

All the above calculations refer to a temperature of 300°K. To calculate the heats of reaction at higher temperatures, eg. 800°K, requires the pertinent heat capacities. These can be computed by group additivity using the data of reference 30. Using the symbol $[]_C$ to denote the heat capacity of a group, we illustrate the calculation for the reaction of example 3.2 above.

$$\Delta C_p(300^\circ K) = [CH_3\cdot]_C + [C\cdot-(C_B)(H)_2]_C - [C-(C)(H)_3]_C - [C-(C_B)(C)(H)_2]_C = 3.26 \text{ cal/g-mol } ^\circ K.$$

The corresponding values at 400,500,600 and 800°K are 2.07,1.32,0.62,0.03. Using these values we obtain

$$\Delta H(800^\circ K) - \Delta H(300^\circ K) = \int_{300}^{800} \Delta C_p(T) dt \approx 0.58 \text{ kcal/g-mol}$$

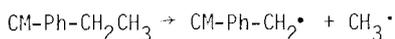
A similar calculation for reaction (D5⁻) gives $\Delta H(800^\circ K) - \Delta H(300^\circ K) = 0.08$. These differences turn out to be quite small.

3.1.2 A-factors

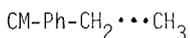
The A-factor is given in terms of the entropy of activation by Eq.(3.2). In gas phase kinetics ΔS^\ddagger can be broken down to contributions from various degrees of freedom which can be estimated by the techniques of ref. 30 as shown in several examples below. However, this procedure cannot be rigorously applied to coal pyrolysis because the reaction medium is an amorphous solid or a viscous liquid, therefore the partition function cannot be factored out as in the ideal gas case. For

certain reactions that can take place in solution as well as in the gas phase it has been found experimentally that as long as the solvent does not play any chemical role, the A-factor in solution was comparable to the A-factor in the gas phase (ref. 34). In a recent study (ref. 35) the rate constants of reactions (D5) and (D8) were estimated to be 0.42 and 1.14 in the liquid and gas phases respectively. However, the experimental data base for these estimates was limited. Moreover, it is not known whether the rough equivalence of rate constants also applies to a condensed phase which is an amorphous solid or a very viscous liquid. In the absence of better information it can still be assumed that A-factors computed for gas phase kinetics are roughly applicable to the coal phase at least when the reactions are not diffusion limited.

In carrying out the detailed calculation of the entropy of activation it must be kept in mind that the reacting functional group is actually attached to a rather bulky molecule. For example, in reaction (D2) Ph is an aromatic nucleus such as naphthalene bridged to other similar units. A more descriptive notation for this reaction then would be

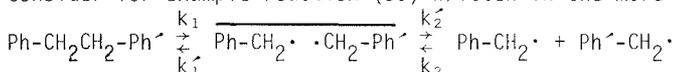


where Ph is connected by one or more bridges to other sections of the coal molecule denoted here as CM. The reactant coal molecule may have molecular weight from one to five thousand or more in the case of pyrolysis but less in the case of hydrolysis and liquefaction. With such large molecular weights the differences between the reactant molecule and the transition state



are small as far as rotational partition functions are concerned. The external symmetry is likewise the same, one, in both reactant and transition state. As a result of the large size and complex nature of the molecule, the main contributions to the entropy of activation come from vibrations, mainly bending modes, and internal rotations.

A persistent difficulty in estimating A-factors for condensed phase reactions is the possibility of diffusional limitations. This difficulty is especially pronounced in coal pyrolysis because of the high viscosity of the condensed phase. Consider for example reaction (D5) written in the more detailed form



where the bar indicates a couple of radicals in close proximity. Because of their bulky size and the high viscosity of the coal phase the two radicals may recombine before diffusing sufficiently apart from each other. This "cage" effect can be analyzed by applying the steady state approximation to the intermediate configuration to obtain for the net dissociation rate the expression

$$r = \frac{k_1 k_2}{k_1' + k_2'} [\text{Ph-CH}_2\text{-CH}_2\text{-Ph}'] - \frac{k_1' k_2'}{k_1' + k_2'} [\text{Ph-CH}_2\cdot][\text{Ph}'\text{-CH}_2\cdot]$$

under diffusion limited conditions $k_1' \gg k_2'$ and the above expression simplifies to $r = k_2' K_1 [\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Ph}'] - k_2 [\text{Ph}-\text{CH}_2'] [\text{Ph}'-\text{CH}_2']$ where $K_1 = k_1/k_1'$. The diffusion parameters k_1, k_2 have been calculated theoretically for the case of polymerization reactions (refs. 36-38). In the case of pyrolysis such theoretical calculations are not feasible. We will return to this subject in the chapter dealing with kinetic modeling.

We shall now present examples of estimation of A-factors for several of the dissociation reactions (D1)-(D8). It should be emphasized once more that the assignment of frequencies to internal rotation and bending modes is subject to a great deal of uncertainty. This is the main reason for the fact that theoretically calculated A-factors can be easily in error by a factor of ten and in some cases more. If on the other hand it is possible to exploit analogies with experimentally known A-factors much more reliable estimates can be obtained. The examples below illustrate the adjustments required in exploiting such analogies. The various frequencies are assigned using the data of ref. 30.

Example 3.6

In this example we will estimate the A-factor of reaction (D2). The starting point is the reaction with Ph an unattached phenyl, Ph_1 , for which the experimental value $\log A = 15.3$ at $1,000^\circ\text{K}$ is given in ref. 29. The estimation of the entropy of activation is based on the change between reactant and transition state,



where the dots indicate the partially broken bond. The contribution of the various degrees of freedom are as follows:

- (i) Translation, spin and symmetry make no contribution as being the same in reactant and transition state.
- (ii) Two principal moments of inertia are increased by a factor of 1.8 with a $R \& n 1.8 = 1.2$ rotational contribution.
- (iii) A C-C stretch ($1,000 \text{ cm}^{-1}$) becomes the reaction coordinate contributing -1.4.
- (iv) The internal rotation about the Ph_1-C bond (barrier changes from 2 to 15 kcal) contributes -1.8; the internal rotation about the CH_2-CH_3 bond (barrier changes from 3 to 0 kcal) contributes 0.2.
- (v) There are four bending modes about the CH_2-CH_3 bond. The frequencies of these modes in the reactant can be estimated by analogy to the aliphatic analog CH_3-CH_3 for which ref. 30 gives $1,000 \text{ cm}^{-1}$. Since the reduced mass of $\text{Ph}-\text{CH}_2\text{CH}_3$ is about two times larger, the associated frequencies are about 700 cm^{-1} . The corresponding frequencies in the transition state can be used as adjustable parameters to bring the estimated total ΔS^\ddagger in accord with the experimental value. The required frequencies turn out to be 210 cm^{-1} .

We now consider the case when Ph is part of a more bulky coal molecule with molecular weight about 500,



The only difference with (d2) is that the contribution of rotation is now negligible. The bending frequencies remain the same because the reduced mass changes by the same factor in the reactant and the transition state. At 1000°K, $\Delta S^\ddagger = 5.7 - 1.2 = 4.5$ and $\log A = 15.0$. Repeating the calculations at 800°K we obtain $\Delta S^\ddagger = 6.4$, $\log A = 15.0$.

Example 3.7

To estimate the A-factor for reaction (D5) we start with the base case



for which ref. 29 gives $\log A = 14.4$ or $\Delta S^\ddagger = 3.0$ at 1000°K. An analysis of ΔS^\ddagger can provide as before a crude estimate for the contribution of the bending modes:

- (i) Translation, spin and symmetry do not change.
- (ii) Rotation: two moments increase by a factor of two contributing $R \ln 2 = 1.4$.
- (iii) A C-C stretch becomes the reaction coordinate contributing -1.4 units.
- (iv) Two internal rotations about the $\text{Ph}_1\text{-C}$ bonds (barrier changes from 2 to 15 kcal) contribute $2 \times (-1.8) = -3.6$ units; an internal rotation about the $\text{CH}_2\text{-CH}_2$ bond becomes a free rotation resulting in an entropy change of 0.2 units.
- (v) To match the experimental $\Delta S^\ddagger = 3$ an additional 6.4 units are needed, which can be assigned to four bending modes. If the frequency of each of these bonds in the reactant is 400 cm^{-1} , the frequency in the transition state must be about 180 cm^{-1}

We now consider the reaction



differing from d_5 mainly in the molecular weight of the group CM-Ph-CH_2 . If this weight is taken as 500 the bending frequencies are $400 (91/500)^{1/2} = 170 \text{ cm}^{-1}$ and $180 (91/500)^{1/4} = 77 \text{ cm}^{-1}$. Using these frequencies and recognizing as before that rotation makes a negligible contribution we find that for 800°K, $\Delta S^\ddagger = 1.1$ and $\log A = 13.9$.

Example 3.8

We now go back to reaction (D4),



where we distinguish the following contributions at 800°K,

- (i) Translation, spin and symmetry do not change.
- (ii) The rotational change is negligible.
- (iii) The internal rotations about the Ph-CH_2 bond and the $\text{CH}_2\text{-Ph}'$ bond contribute -2.1 and 0.2 units, respectively.
- (iv) The four bending modes will be taken as in the previous example 170 cm^{-1} in the reactant and 77 cm^{-1} in the transition state making a contribution of 4×1.5

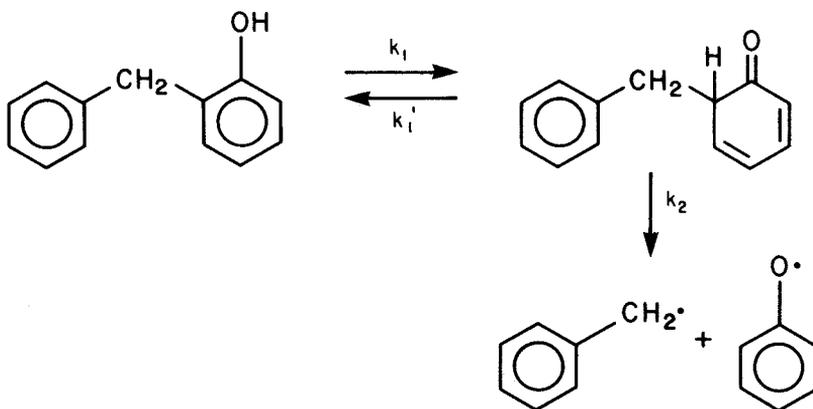
= 6 units. The sum of these components is $\Delta S^{\ddagger} = 3.0$ and $\log A = 14.3$.

We have analyzed, rather crudely, the reactions (D2), (D4) and (D5). The A-factor for (D1) is estimated by adjusting the experimental value of $\log A = 15.5$ at 1000°K reported for the dissociation of toluene. The A-factors of (D6)-(D8) can be assumed to be approximately equal to those of (D2)-(D5) respectively. The results of these estimates are all listed in the last table of the chapter.

3.1.3 The effect of phenolic hydroxyl groups

It was mentioned earlier that phenolic hydroxyl groups have a profound effect on the rates of dissociation reactions. The reactions under consideration are $\text{HO-Ph-CH}_2\text{-X} \rightarrow \text{HO-Ph-CH}_2\cdot + \text{X}\cdot$ where the -OH is ortho or para to the benzylic carbon and X is one of the groups H, CH₃, Ph, CH₂-Ph. In an early study (ref. 33) of cresol pyrolysis, o-cresol and p-cresol were found to decompose about four times faster than m-cresol at 816°K. The rate determining step in each case was the dissociation of a benzylic H atom. Assuming equal A-factors, the activation energy of the first two reactions must have been about 3 kcal lower than that of the last reaction. Although not examined in this study, the dissociation of the benzylic hydrogen in toluene and m-cresol must have very similar activation energies.

The activating mechanism of ortho or para situated hydroxyl was recently identified as due to a keto-enol tautomerism (ref. 39),



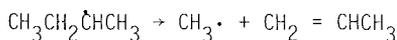
Assuming the second step to be rate determining, the effective reaction rate constant is k_2k_1/k_1' . The activation energy of step 2 was estimated as about only 45 kcal/g-mol while the equilibrium constant k_1/k_1' was estimated as 10^{-6} at 400°C. Assuming an A-factor equal to that of bibenzyl dissociation, the effective rate constant k_2k_1/k_1' turns out to be several orders of magnitude larger than that of direct dissociation.

3.2 DISSOCIATION OF FREE RADICALS

The following are representative of this class of reactions:



Among the above reactions (DB1), (DB2) and (DB4) involve the conversion of an alpha radical to a higher energy radical. The attendant loss of resonance stabilization energy results in a higher activation energy compared to the corresponding aliphatic analog. For example reaction (DB2) has an activation energy of 45 compared to 34 for the aliphatic analog



The exception is reaction (DB3) where resonance stabilization energy is gained and the activation energy is very low (9.6). The examples below focus on the estimation of A-factors, using the same techniques as in section 3.1.2. The estimation of activation energies can be carried out in a straightforward way by group additivity and is illustrated only in example 3.9.

Example 3.9

We start with reaction (DB1) and compare



with the aliphatic analog



for which the experimental value $\log A = 14.3$ at 500°K is reported (ref. 29). The two reactions differ mainly in the internal rotation, Ph-CH bond vs. CH_3 -CH bond. Taking this difference into account and adjusting for the temperature yields $\log A = 15.1$ at 800°K .

Example 3.10

We next consider reaction (DB2). The heat of reaction can be immediately calculated by group additivity using the group values of ref. 30 as $\Delta H = 37.8$. The activation energy is given by $E = \Delta H + E'$ where E' is that of the reverse reaction. The latter is about 7.2, section 3.5, therefore $E = 45$.

To estimate the A-factor we consider the entropy changes associated with



and the aliphatic analog

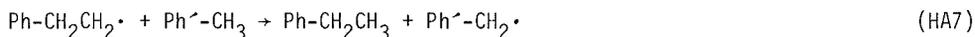


for which ref. 29 gives the experimental value $\log A = 14.2$ at 570°K . The difference in the entropies of (db2) and (db2') is mainly due to (i) rotation which contributes to (db2') but not (db2) and (ii) internal rotation in (db2) is about the Ph-C bond while in (db2') is about the CH_3 -C bond. The differences due to (i) and (ii) nearly cancel each other so that for (db2), $\log A = 14.2$ at 570°K and $\log A = 14.4$ at 800°K .

with the standard state being at pressure $p_0 = 1$ at. For the entropy change of -34.2, $\log A = 8.4$ ℓ/s g-mol.

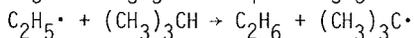
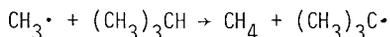
3.4 HYDROGEN ABSTRACTION

The following are a few representative reactions



The activation energies of (HA1), (HA2) have been estimated as 2.3, 8 by a variant of the bond-order-bond-energy method (ref. 40). The activation energy of (HA3) can be estimated by analogy to suitable aliphatic analogs as follows.

The two reactions



have activation energies 8 and 8.9 respectively. The difference of 0.9 is assumed to apply to the reactions (HA2) and (HA2) as well, producing the estimate 8.9 for (HA2).

The activation energies of reactions (HA4)-(HA6) are taken equal to those of their aliphatic analogs. For example, the aliphatic analog of (HA5) is



Finally, the activation energy of (HA7) is taken equal to that of (HA3).

The estimation of A-factors for hydrogen abstraction reactions is illustrated by the following two examples.

Example 3.13

The transition relevant to (HA1) is



By definition, the entropy of this transition is

$$\Delta S^\ddagger = S^\ddagger - S^\circ(\text{R}) - S^\circ(\text{H}^\bullet)$$

where R represents CM-Ph-CH₃. The difference $S^\ddagger - S^\circ(\text{R})$ has the following components

- (i) Translation, external symmetry and rotation zero or negligible.
- (ii) Spin from 2 to 1 with contribution $R \ln 2$.
- (iii) The barrier for internal rotation about the Ph-C bond changes from 0 to 7.5 kcal contributing -1.3 units. At the same time a loss of a symmetry factor of 3

associated with internal rotation contributes $R \ln 3$ units.

(iv) A C-H stretch becomes reaction coordinate causing an entropy change of -0.1. A new H...H stretch (2800 cm^{-1}) contributes 0.1.

(v) Two new H...H...C bends (1000 cm^{-1}) contribute $2 \times 1.1 = 2.2$.

(vi) Two H-C-H Bends (1400 cm^{-1}) become H...C-H bends (1000 cm^{-1}) causing an entropy change of $2 \times 0.5 = 1$.

The resultant of these components is $S^\circ^\ddagger - S^\circ(R) = 5.5$. At the same time standard tables (ref. 30) give $S^\circ(\text{H}\cdot) = 32.3$ so that $\Delta S^\circ^\ddagger = -26.8$ and $\log A = 10.0$.

The A-factors of reactions HA2 and HA3 are best estimated by comparison with aliphatic analog reactions

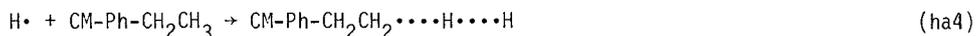


The experimental $\log A$ for these reactions are 11.0, 8.5, 8.0 at 400°K (ref. 30).

Assuming that $\log A(\text{HA}_i) - \log A(\text{HA}_1) = \log A(\text{HA}_i') - \log A(\text{HA}_1')$ for $i = 1, 2, 3$ and that each difference is independent of temperature we obtain for 800°K the crude estimates $\log A(\text{HA}_2) = 7.5$, $\log A(\text{HA}_3) = 7.0$.

Example 3.14

For reaction (HA4) we need the entropy change of

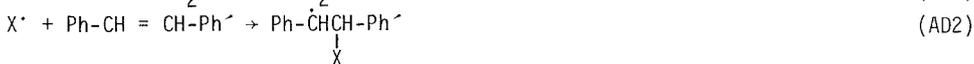


This change can be calculated by analogy to (ha1) from which it differs only by the fact that the barrier for internal rotation about the Ph-C bond does not change. Therefore, we set $\Delta S^\circ^\ddagger(\text{HA}_4) = \Delta S^\circ^\ddagger(\text{HA}_1) + 1.3 = 25.5$ and $\log A(\text{HA}_4) = 10.3$.

Reactions (HA5) and (HA6) can be treated similarly to (HA2) and (HA3). The result is $\log A(\text{HA}_5) = 7.8$, $\log A(\text{HA}_6) = 7.3$. Finally, in the absence of any other information we can crudely set $\log A(\text{HA}_7) = \log A(\text{HA}_6)$.

3.5 ADDITION OF RADICALS TO DOUBLE BONDS

These reactions are the reverse of (DB1)-(DB4) and may be exemplified by:



where $\text{X} = \text{H}, \text{CH}_3$ or C_2H_5 . The activation energies of (A1) and (A2) can be approximated by those of the aliphatic analogs



These are listed in the compendium of Kerr and Parsonage (ref. 41) as 1.2, 7.2, 7.3 for (AD1') with $\text{X} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$, respectively. The corresponding values for (AD2') are listed as 4.3, 7.5, 8.5.

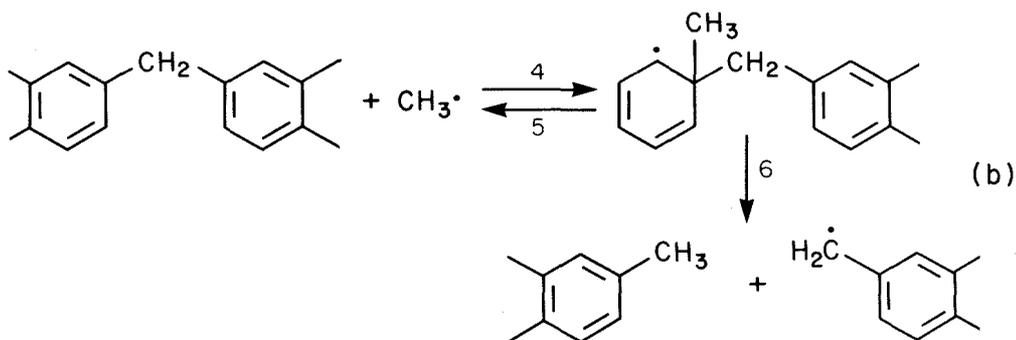
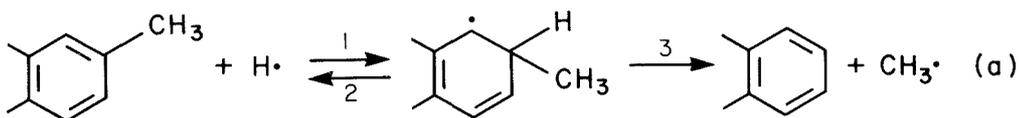
The entropies of activation of (AD1) and (AD2) can be calculated from the entropy of reaction and the activation entropy of the reverse reaction. Taking as an example (AD1) with $X = \text{CH}_3$ we have

$$\Delta S^\ddagger(\text{AD1}) = \Delta S^\ddagger(\text{DB2}) + \Delta S^\circ(\text{AD1})$$

Using group additivity we calculate for 800°K $\Delta S^\circ = -33.7$ so that $\Delta S^\ddagger(\text{AD1}) = 3.4 - 33.7 = -30.3$, $\log A = 9.3$.

3.6 ADDITION OF RADICALS TO AROMATIC RINGS

The limited literature on the addition of small radicals like CH_3^\cdot and $\text{C}_2\text{H}_5^\cdot$ to aromatic rings has been reviewed by Szwarc et al. (refs. 42,43) and Williams (ref. 44). The reaction mechanism consists of addition to the aromatic ring to form a cyclohexadiene intermediate followed by dissociation as shown in the following two examples:



Addition reactions have been studied in solution wherein methyl and other carbon-centered radicals were produced by the decomposition of initiators like acetyl peroxide. Hydrogen addition has not been studied as such because it cannot be produced in solution in any clean-cut fashion. However, hydrogen addition at temperatures higher than 400°C has been identified as an important step in the thermal reactions of various aromatic compounds (ref. 33,45).

When addition takes place in solution at modest temperatures, the intermediate cyclohexadiene radical can recombine with other radicals or abstract hydrogen leading to a variety of products. At temperatures representative of coal pyrolysis (above 400°C) the decomposition steps 2 or 3 in (a) or 5,6 in (b) would be quite rapid to effectively suppress recombination reactions. Because of the larger energy of H^\cdot compared to CH_3^\cdot the decomposition step 3 is much faster than (2) and reaction

(a) is kinetically equivalent to

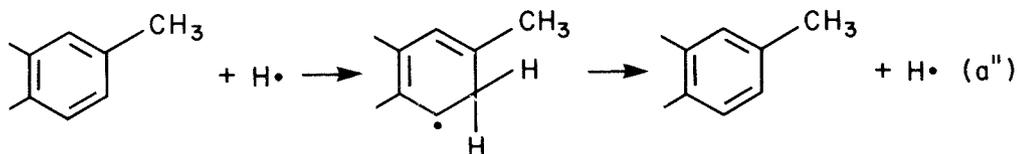


Likewise, as a result of the higher stability of the benzyl radical



Because reactions (a) or (b) often follow the route (a') or (b') they are sometimes characterized by the terms aromatic substitution or displacement reactions.

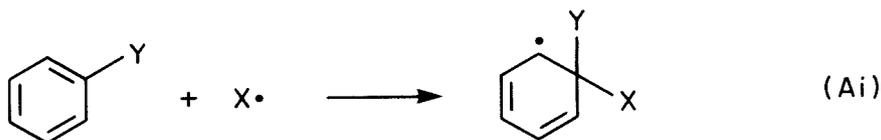
Returning to reaction (a) we note that the addition of the hydrogen atom can take place at other positions, for example



This reaction is obviously kinetically insignificant. Inasmuch as reported experimental values for the rate constants of addition reactions refer to addition at any position around the ring, these constants should be suitably reduced if addition at a specific site is considered. Unfortunately, the relative addition rates at positions like (a) and (a'') have not yet been measured.

In coal pyrolysis, reactions of the type (a) can be the source of various hydrocarbon gases via the corresponding radicals. For example the $\text{CH}_3\cdot$ radical produced in (a) will evolve as methane after hydrogen abstraction from some suitable site. Reaction (b) is important as a low activation energy route to the dissociation of methylene bridges.

The rate parameters in Table 3.2 refer to addition to the benzene ring



where $X = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$ ($i=1,2,3$) and Y is H or an alkyl chain or bridge. Depending on the relative stability of $X\cdot$ and $Y\cdot$, the decomposition of the cyclohexadiene radical would lead to the product PhX or back to the reactant PhY . At high temperatures the dissociation of the hexadiene radical is relatively rapid so that the overall reaction is controlled by the rate of the addition step. The activation energies of the addition reactions are in the range 0-8 (ref.30), probably close to 8 for $\text{CH}_3\cdot$ and $\text{C}_2\text{H}_5\cdot$ and about 2-4 for $\text{H}\cdot$. The parameter values listed in Table 3.2 refer to the benzene ring. It must be noted that the rates of addition increase with increasing size and decreasing stability of the aromatic ring system. Szwarc and Binks (ref.43) report relative rates of 1,22,27 and 280 for the addition of methyl radical to benzene, naphthalene, phenanthrene and anthracene, respect-

ively. The rate constants must obviously be adjusted upwards when applied to kinetic modeling of coal reactions.

3.7 REACTIONS OF CARBOXYL AND PHENOLIC HYDROXYL GROUPS

Among the principal products of pyrolysis, water and carbon dioxide are generally attributed to the phenolic hydroxyl and carboxyl groups in coal. Brooks et al. (ref.46) used IR spectroscopy and wet chemical methods to measure the concentration of oxygen groups in brown coals undergoing pyrolysis and suggested that at temperatures below 300°C water is produced by esterification reactions presumably of the type



At temperatures between 300 and 450°C they observed a further decrease of phenolic -OH by reactions of the type



of which (iii) was singled out as more important. At the same time, ester groups formed by (i) were found to decompose with the elimination of carbon dioxide,



Presumably, free carboxyl groups would also decompose under these conditions.

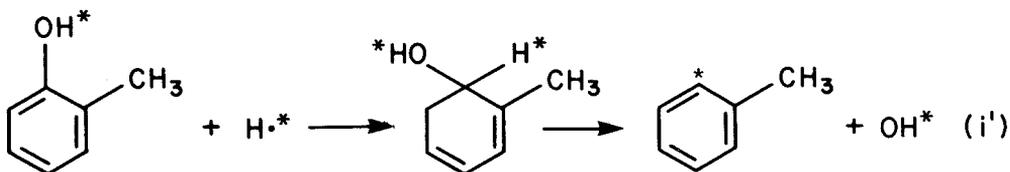
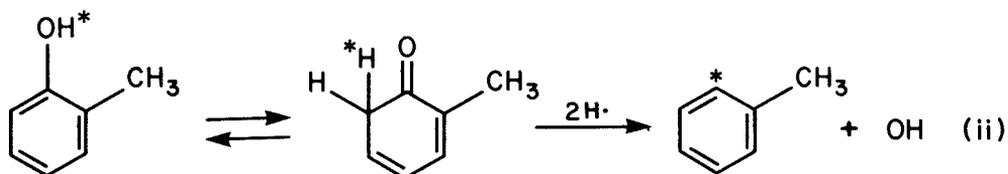
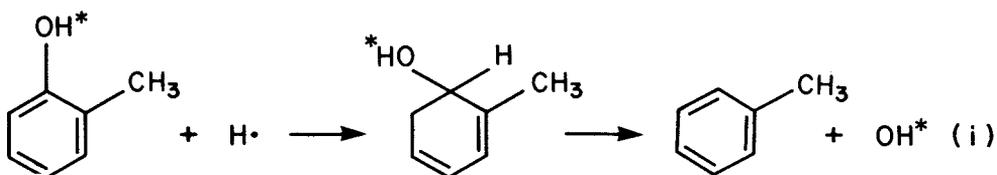
Reactions (i)-(iii) are significant not only as sources of "chemical water" but as producing additional linkages among the structural units resulting in a suppression of tar formation. Since the content of hydroxyl and carboxyl groups is higher in coals of low rank, the above condensation reactions offer an explanation for the low amount of tar produced in the pyrolysis of subbituminous coals and lignites. The kinetics of the condensation reactions (i)-(iii) have not been studied at the temperatures of interest to pyrolysis (above 400°C). Moreover, the experimental evidence has not as yet been sufficient to distinguish which of these three reactions is more important.

At temperatures above 600°C the reactions of hydroxyl groups become more complex leading to a variety of products including carbon monoxide. While all reactions discussed in sections 3.1-3.6 were free radical in nature, the high temperature reactions involving phenolic hydroxyls are believed to largely proceed by concerted mechanisms. The remainder of the chapter is a survey of concerted mechanisms relative to the thermal reactions of coal.

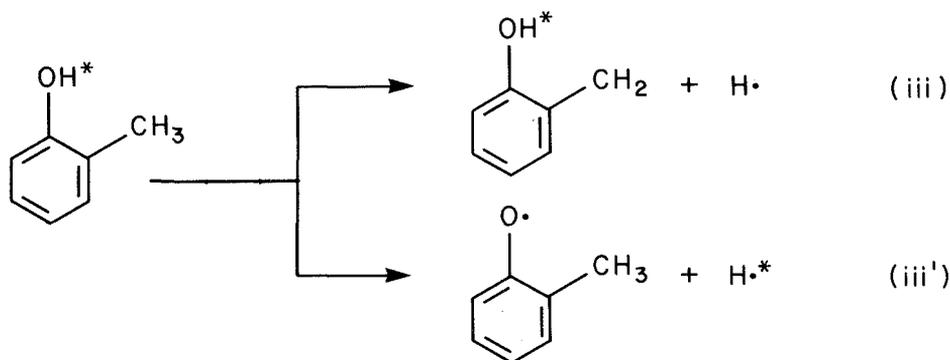
Concerted Reactions

The term "concerted" indicates reactions that involve simultaneous breaking (and making) of more than one bond. By contrast, the free radical reactions surveyed so far involve the breaking (and making) of one bond at a time. The following examples drawn from model compound studies give an idea of the role of concerted reactions in coal pyrolysis.

Cypres and Betten (refs. 47-49) studied the pyrolysis of phenol, o-cresol and p-cresol labelled at specific positions by ^{14}C and ^3H . The reactions were carried out in the temperature range 700-900°C and resulted in a wide variety of products. For example, in the pyrolysis of one mole of o-cresol at 750°C for 2.5 seconds, the major products (in moles) were 0.064 benzene, 0.034 toluene, 0.242 phenol, 0.10 water, 0.139 carbon monoxide, 0.128 methane, 0.078 hydrogen and 0.032 char. When the o-cresol was tritiated on the hydroxyl group, the toluene contained a considerable amount of tritium while the water contained 0.61 atoms of tritium. This distribution of tritium was interpreted as evidence against the free radical mechanism (i) which would produce toluene free of tritium. Instead, the authors proposed the concerted mechanism (ii) which produces tritiated toluene. This explanation is not complete, however, since the elimination of oxygen in the last step of (ii) is not mechanistically satisfactory as written down and, in addition, it does not explain the formation of a considerable amount of tritiated water. Mechanism (i) can partially explain the formation of tritiated toluene and water if $\text{H}\cdot$ is replaced by $\text{H}\cdot^*$ as shown in (i')

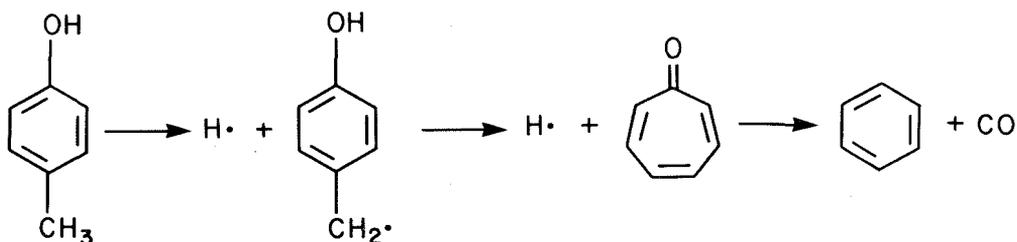


The relevant issue in choosing between (ii) and (i) is the relative rates of the two reactions producing hydrogen atoms:



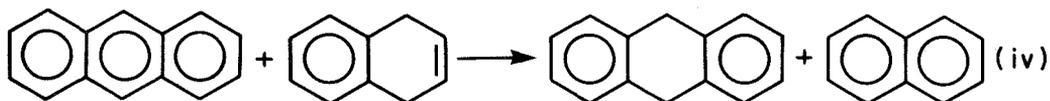
Mechanism (ii) provides a better explanation of the products when (iii) is faster than (iii') while (i') becomes more credible when (iii') is faster. Unfortunately the relative rates of (iii) and (iii') have not been determined independently. Another possible explanation is hydrogen exchange (scrambling) whereby the tritium atom is spread around the ring preceding dissociation. It appears that the experimental data available are not sufficient to discriminate between the free radical and the concerted mechanisms.

To explain the formation of carbon monoxide the authors of refs. 47-49 suggested two possible schemes, one of which involves a seven-membered ring,

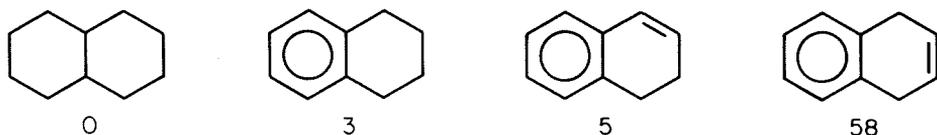


Independently of the validity of this particular mechanism, it is clear that the formation of carbon monoxide requires the disruption of the benzene ring and cannot be explained solely by free radical steps. It should be noted in this connection that carbon monoxide appears in significant amounts only when the pyrolysis temperature exceeds 700°C.

In an attempt to demonstrate the importance of pericyclic pathways in the thermal reactions of coal, Virk et al. (ref.50) studied the hydrogenation of anthracene, phenanthrene and a high volatile bituminous coal with various hydrogen donor solvents at 300°C for two hours. One of the reactions studied was

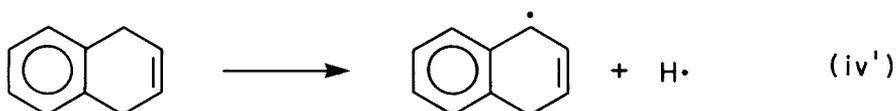


The percentage conversion obtained with different H-donor solvents was as follows:



The large difference with the last two solvents was explained by the Woodward-Hoffman rules governing concerted reactions.

It must be noted that if reaction (iv) were to take place by a free radical mechanism it would require as a first step the dissociation of a hydrogen atom from the H-donor molecule:



This reaction has activation energy about 69 kcal, therefore would be extremely slow at 300°C. Using stereospecificity properties, von E. Doering and Rosenthal (ref. 51) demonstrated a concerted path for the thermal decomposition of *cis*-9,10-dihydronaphthalene to naphthalene, tetralin and hydrogen.

Several authors who have studied the pyrolysis of tetralin or the dissociation of bibenzyl in tetralin (refs. 52-54) have explained their results solely by free radical mechanisms. More experimental work is needed, preferably with labelled compounds, to determine which of the pyrolysis reactions proceed by concerted mechanisms and which by the more widely accepted free radical mechanisms.

TABLE 3.2 Rate parameters of selected elementary reactions at 800°K

| | $\log_{10}A$ | | E | |
|----|--------------------------------------|----|--------------|---|
| | (A in s ⁻¹ or lt/g-mol s) | | (kcal/g-mol) | |
| D1 | 14.9 | BN | 85.3 | G |
| D2 | 15.3 | BN | 72.4 | G |
| D3 | 15.4 | BN | 69.5 | G |
| D4 | 14.3 | G | 80.7 | G |
| D5 | 13.9 | BN | 56.4 | G |
| D6 | 15.3 | G | 68.6 | G |
| D7 | 14.3 | G | 85.5 | G |
| D8 | 13.9 | G | 55.6 | G |

| | | | | |
|-----|---------------|---|------|-----|
| DB1 | 15.1 | G | 51.7 | G |
| DB2 | 14.4 | G | 45.0 | G |
| DB3 | 14.2 | G | 9.6 | G |
| DB4 | 12.8 | G | 50.2 | G |
| Rxn | $\log_{10} A$ | | E | |
| R1 | 8.4 | | 0 | |
| HA1 | 10.0 | G | 2.3 | ZM |
| HA2 | 7.5 | G | 8.0 | ZM |
| HA3 | 7.0 | G | 8.9 | G |
| HA4 | 10.3 | G | 9.7 | BTK |
| HA5 | 7.8 | G | 10.8 | BTK |
| HA6 | 7.3 | G | 13.4 | ZM |
| HA7 | 7.0 | G | 8.9 | G |
| AD1 | | | | |
| X=1 | 11.0 | G | 1.2 | G |
| 2 | 9.3 | G | 7.2 | G |
| 3 | 9.2 | G | 7.3 | G |
| AD2 | | | | |
| X=1 | -- | | 4.3 | G |
| 2 | -- | | 7.5 | G |
| 3 | -- | | 8.5 | G |
| A1 | | | | |
| X=1 | 9.3 | G | 1.2 | KP |
| 2 | 7.3 | G | 7.2 | KP |
| 3 | 7.3 | G | 7.3 | KP |

BN: ref. 29

BTK: ref. 30

G: estimated by the author

KP: ref. 41

ZM: ref. 40