

flight instrument, and it should in principle be possible to use laser and plasma desorption alternatively in the same instrument. With electrospray ionization of proteins, a series of peaks in the  $m/z$  900-1200 range is observed. These peaks represent highly charged molecular ion species and can be used to calculate the corresponding molecular weight of the protein.<sup>54</sup> Proteins up to 60 kDa have been analyzed with this technique,<sup>55</sup> but the upper limit is not known.

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In conclusion, PDMS is already a valuable tool for the protein chemist, and there seems to be room for improvements and for combining PDMS with other techniques and, thus, for increasing the practical applicability of mass spectrometry in the future.

*Sincere gratitude is expressed to graduate students and postdoctoral collaborators whose names are cited in the references. A special thank-you to Professor B. Sundqvist, Uppsala University, who introduced me to the world of sputtering of large molecules. Support for our work has been provided by the Danish Technical Science and Natural Science Research Councils.*

## Coal Pyrolysis

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### Introduction

Coals are composed of fossil plant materials that have been subjected to chemical and biochemical decay before burial and to pressure and heating after burial.<sup>1</sup> The components of the plants decompose at different rates depending on their chemical constitution and the environment in which they are deposited. The organic components transform into a collection of petrographically distinct materials known as macerals.<sup>2</sup> These substances, which occur in three distinct groups, the liptinites, the vitrinites, and the inertinites, are photogenetic organic entities or optically homogeneous aggregates of phylogenetic entities possessing distinctive chemical and physical properties.<sup>3</sup> The vitrinites, which are derived for the most part from the lignin in wood, are the principal constituents of most coals. Consequently, the vitrinite-rich coals have received a proportionally significant share of scientific and technological attention.

Although neither the macerals nor the coals have a chemical structure in the conventional sense of the term, several workers in the field have proposed working hypotheses that account for the spectroscopic information such as the solid state proton and carbon magnetic resonance spectral data<sup>4</sup> and for chemical observations such as the substances obtained in supercritical extraction experiments<sup>5</sup> or in carefully designed oxidation reactions.<sup>6</sup> A contemporary representation of an often-studied bituminous coal from the Illinois No. 6 seam is shown in Figure 1.<sup>7</sup>

Considerable technological progress in coal utilization has been made in recent years, with two new major gasification installations in operation in the United

States. One at Coolwater, CA, produces gas turbine fuels for power generation;<sup>8</sup> the other, at Grand Forks, ND, produces methane.<sup>9</sup> It is now well appreciated in the technological community that the discovery of new, more economically feasible methods for the fuller utilization of coal in the United States for energy generation, transportation fuels, chemical feedstocks, and other related purposes will require a rather thorough appreciation of the chemical nature of its constituents and their patterns of reactivity. It is equally well appreciated in the scientific and engineering communities that the achievement of these objectives is an exceedingly challenging intellectual problem. Chemists who, generally speaking, are accustomed to carefully designed investigations of the behavior of pure substances in carefully controlled environments are challenged by the enormous complexity of coal chemistry.

Virtually all of the technologically important processes such as liquefaction, in which coal is converted into substances that may be recovered by distillation, and gasification, in which coal is converted into substances that are volatile, begin with thermal reactions that involve deep-seated molecular transformations. The thermal decomposition reactions of the coal macromolecules that occur during the earliest stages of

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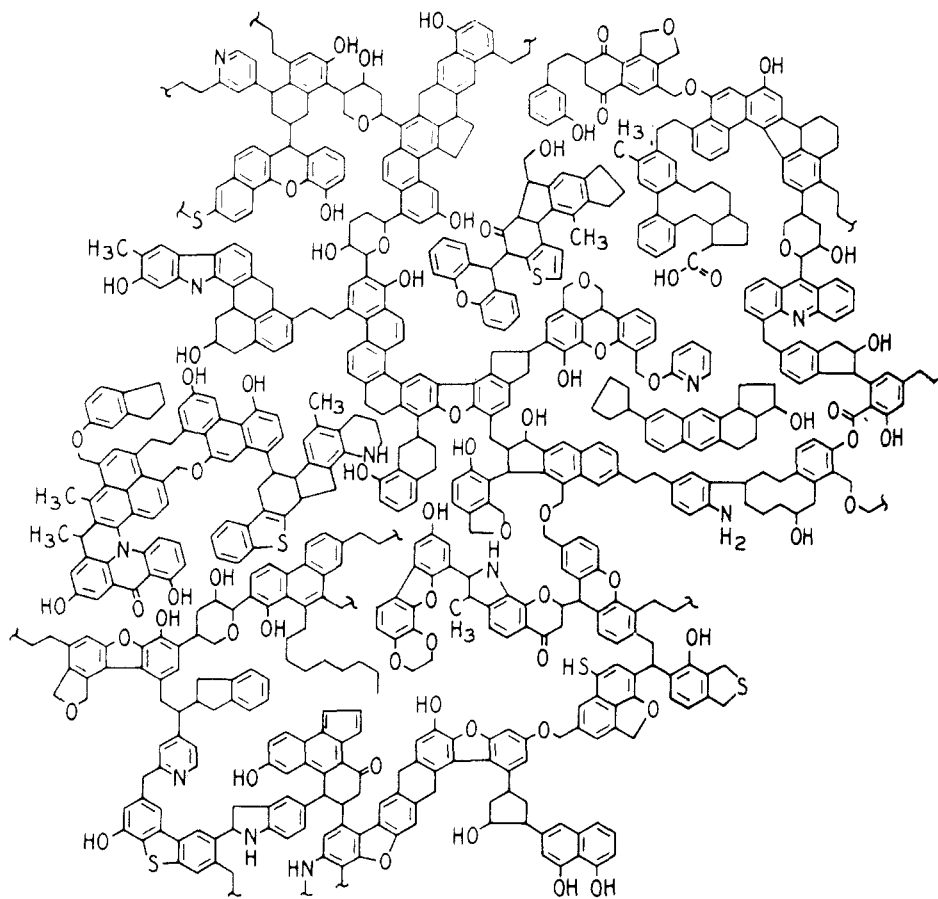
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Leon M. Stock was born in Detroit, MI, in 1930. He received his B.S. in Chemistry from the University of Michigan in 1952. After two years in the U.S. Army, he continued his education at Purdue University, where he received his Ph.D. degree in 1959 under the direction of Herbert C. Brown. He is now Professor of Chemistry at The University of Chicago and Director of the Chemistry Division of Argonne National Laboratory. He received the H. H. Storch Award of the American Chemical Society for his work in coal chemistry in 1987.



**Figure 1.** Shinn's conception of the composition of a high-volatile bituminous coal.<sup>7</sup> Smaller extractable molecules are trapped within a major macromolecular network that extends ( $\sim$ ) in three dimensions.

these processes are essential first steps in this chemistry. Many of the same pyrolytic reactions are basic processes in combustion. Efforts in gasification research have focused, understandably, on the development of information to describe the impact of process variables on conversion.<sup>10</sup> Excellent work has been done on the effects of temperature, pressure, heating rate, particle size, and coal type on the reaction rates and product distributions.<sup>11</sup> Important effort continues to be directed to the assessment of the factors governing the rate of evolution of certain small gaseous molecules of known structure and the rate of production of other volatile substances that constitute the tar and distill from the coal during the reaction.<sup>13-15</sup> However, while investigations of this kind are essential, they do not yield direct information about the chemical processes that control the reaction velocity or about the actual molecules responsible for the formation of the products. Failure to achieve a greater understanding of this issue continues to impede attempts to model the pyrolysis accurately and to design unambiguous strategies for

more effective combustion, liquefaction, or gasification.

Chemists and engineers interested in these pyrolytic reactions and in the development of a more secure understanding of the basic reactions by which substances of the kind shown in Figure 1 could be converted into much simpler gaseous compounds have been forced by circumstances to adopt one of two undesirable procedures. Either they have investigated coals or they have investigated pure compounds, usually relatively simple molecules, that were thought to be representative of the behavior of coal. The first approach is hampered by the lack of information concerning the structural elements of coal that actually undergo reaction. The second approach is easily accomplished experimentally and provides information that can readily be discussed, but there is no secure basis for the extrapolation of the information obtained in these studies to the chemistry that occurs within the coal particles during pyrolysis. Clearly, the complex heterogeneous reaction medium of the coal particle is very different from the medium, usually a homogeneous phase, used for the model compound investigations. Further, the medium changes as the reaction proceeds. The coal molecules are large and essentially immobile in the first stages of pyrolysis. They undergo several phase transitions during the pyrolysis prior to resolidification in the last stages of the reaction. These physical changes are accompanied by even more significant chemical changes, the most important of which involves the variable nature of the hydrogen donor groups as the reaction proceeds. In essence, the coal systems are too complex and the model compound systems are too simple. We have been

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Table I  
Hydroxyl Groups in Illinois No. 6 Coal Extract<sup>17</sup>

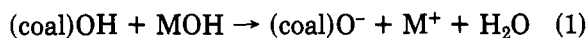
structural element	abundance/100 mol of C
primary aliphatic alcohol	0.1
unhindered phenol	2.8
hindered phenol	0.7
aryl 1,2-dihydroxyl compound	0.4

working on an alternate approach to the examination of the issue of coal reactivity. Specifically, we have adopted an approach in which a known, often isotopically labeled structural element is covalently incorporated into the coal and the modified coal is subjected to conversion reactions to define the behavior of the structural fragment in the same reaction system, i.e., the coal that is the subject of the inquiry. In this way, the reactivity patterns of different molecular fragments can be worked out and the principal reaction pathways of reactive intermediates can be ascertained. Many of the conclusions reached in the course of our studies secure suggestions that have been advanced by other workers in the field. In other cases, the studies yielded distinctly different insights concerning the reaction pathways.

### Coal Alkylation

Two bituminous Illinois No. 6 coals, one of which was obtained from the premium sample program of The Argonne National Laboratory, were used. The elemental formula,  $C_{100}H_{87.9}N_{1.5}S_{1.3}O_{8.8}$ , indicates its heteroatom-rich nature. Davidson reviewed the early structural work on oxygen compounds,<sup>16</sup> and additional information has recently been presented.<sup>17</sup> In brief, approximately 50% of the oxygen atoms in Illinois No. 6 coal occur in phenolic hydroxyl groups, Table I. The most recent solid state magnetic resonance data imply that this coal is free of carbonyl groups,<sup>18</sup> but other, more direct techniques suggest that 5–10% of the oxygen atoms appear in carboxyl groups.<sup>17</sup> The remainder appear in ethers, the chemical behavior of which suggests that dibenzo- and naphthobenzofurans and xanthenes predominate.

This knowledge prompted the use of O-alkylation to modify the coals. The O-alkylation reaction worked out by Liotta and his associates proved suitable.<sup>19,20</sup> Many coals can be selectively alkylated in tetrahydrofuran by this method with tetrabutylammonium hydroxide and primary alkyl halides, eq 1 and 2. Tetrabutyl-



ammonium ion, although a superior phase-transfer agent, can be tenaciously retained in the modified coals and can produce hydrocarbons during pyrolysis. It was replaced with potassium hydroxide.<sup>21</sup> Certain primary alkyl halides such as 2-phenylethyl bromide undergo elimination. This difficulty was avoided by the use of alkyl tosylates.<sup>21</sup>

Techniques of this kind were used to prepare O-substituted coals with simple alkyl, allyl, and arylmethyl groups, structures with aromatic and hydroaromatic fragments, and their <sup>2</sup>H- and <sup>13</sup>C-labeled derivatives. Both known methods and newly developed selective exchange reactions were used for the preparation of the labeled alkylating agents.<sup>22,23</sup> A new procedure was worked out for the preparation of C-substituted coals.<sup>21</sup> The reactive hydroxyl groups were blocked by methylation, the exhaustively methylated coal was then C-alkylated, and the blocking methyl groups were removed by lithium iodide.<sup>24</sup>

### Pyrolysis

The wire grid reactor developed by Anthony and co-workers<sup>25</sup> was used because a broad range of experimental conditions could be achieved. This reaction system was especially attractive since the experiments could be performed with small quantities of alkylated coals. The small samples and the small coal particle sizes used with the wire grid reactor ensure, insofar as possible, that chemical kinetics rather than heat or mass transfer phenomena are rate controlling. Secondary gas-phase reactions are effectively eliminated because the surrounding gaseous environment remains essentially at room temperature. In a typical experiment, 10–15 mg of coal was placed on a preconditioned 325-mesh, 316 stainless steel screen clamped between two electrodes. The reactor was sealed and flushed with helium. Then, the pressure in the reactor was adjusted to 0.02 MPa and the sample was heated at 1000 °C s<sup>-1</sup> to the desired final temperature, usually between 600 and 800 °C. After the reaction system had cooled to ambient temperature, the gaseous products were absorbed on a Tenax column and analyzed by gas chromatography-mass spectroscopy.

In the first investigations, we examined the pyrolysis of isotopically labeled and unlabeled O- and C-benzylated Illinois No. 6 coal to establish the utility of the wire grid reactor system and the modified-coal strategy.<sup>24</sup> We found that the char, tar, and gas yields for the modified coals were comparable with the results that have been obtained for unmodified coals under similar conditions.<sup>24,26</sup> Thus, the introduction of the benzyl groups into the coal did not unduly perturb the behavior of the original coal. We also found that the deuterium and carbon labels from the benzyl groups were distributed among the gaseous products in specific, interpretable ways. Hence, the labels could be used to trace the reactions. It was also clear that the reactions proceeded rather selectively even at the high temperatures used in these experiments. These features imply that the reactions within the coal particles are kinetically controlled processes.

### The Origins of Methane

The origins of methane and the other gaseous products provide considerable information about the patterns of pyrolysis in bituminous coals. Accordingly, this

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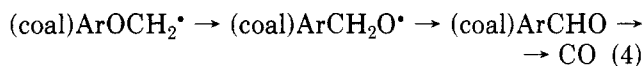
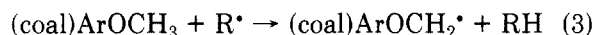
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feature will be stressed in this overview. Our work began with a recognition of the fact that methane and the other gaseous products are formed at discontinuous rates. This feature was beautifully illustrated by Juntgen and his associates.<sup>13</sup> They heated several representative German coals at 3 °C min<sup>-1</sup> to 950 °C under dinitrogen and observed that plots of the rate of formation of methane versus the temperature exhibited two to four distinct maxima.<sup>13</sup> Their observations are in accord with information provided independently by Suuberg.<sup>26</sup> Results of this kind suggest that methane is formed from several structurally different precursors, and Solomon proposed that methane could be formed from methoxy groups, from methyl groups bonded to aromatic rings, and from high molecular weight paraffinic compounds.<sup>14</sup> We conducted pyrolysis experiments with selected modified coals to gain further information on the reaction pathways.

**Methoxy Groups.** Methoxy groups are present in abundance in lignin, the principal precursor of coal.<sup>27</sup> These reactive substituent groups disappear as coals mature. Thus, methoxy groups are present in young lignites, but they are absent from most bituminous coals such as Illinois No. 6. However, the fact that *O*-methyl groups can be readily reintroduced into this coal provided an opportunity to investigate their pyrolysis chemistry.

The pyrolysis of *O*-methyl Illinois No. 6 and *O*-methyl Wyodak coals has been investigated in several laboratories.<sup>28-30</sup> The observations that have been obtained in these investigations are quite comparable. For example, all the studies indicate that the *O*-methyl coals provide greater yields of methane than the unmodified coals. Results of this kind are compatible with the view that the methoxy groups are methane precursors, but the results for the *O*-methyl-<sup>13</sup>C coals are especially informative.<sup>30</sup> In this case, approximately 25% of the *O*-methyl-<sup>13</sup>C groups decompose during the rapid pyrolysis. The carbon atoms appear in methane (78%), ethane (2%), carbon monoxide (14%), methanol (4.5%), and carbon dioxide (1.5%).<sup>30</sup> The high yield of methane-<sup>13</sup>C establishes that simple carbon-oxygen bond cleavage is the dominant reaction, but the detection of labeled carbon monoxide indicates that the reaction pathway, eq 3 and 4, which was proposed by



Schlosberg and co-workers, plays a clear role.<sup>31-34</sup> Labeled methanol can arise from several sources, the most important of which is the decomposition of small quantities of methyl esters in Wyodak coal, and the labeled carbon dioxide may signal a role for the water

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**Table II**  
Distribution of Labeled Products Observed for the  
Pyrolysis of *O*-1-(Octadecyl-*d*<sub>37</sub>) Illinois No. 6 Coal

yield, mol/100 mol of carbon					
methanes		ethanes		ethenes	
CH <sub>4</sub>	5.8	C <sub>2</sub> H <sub>6</sub>	0.40	C <sub>2</sub> H <sub>4</sub>	0.62
CH <sub>3</sub> D	0.23	C <sub>2</sub> H <sub>5</sub> D	0.036	C <sub>2</sub> H <sub>3</sub> D	0.018
CH <sub>2</sub> D <sub>2</sub>	0	C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	0.028	C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	0.013
CHD <sub>3</sub>	0	C <sub>2</sub> H <sub>3</sub> D <sub>3</sub>	trace	C <sub>2</sub> HD <sub>3</sub>	0.056
CD <sub>4</sub>	0	C <sub>2</sub> H <sub>2</sub> D <sub>4</sub>	0.012	C <sub>2</sub> D <sub>4</sub>	0.18

gas shift reaction.<sup>30</sup> Our observations clearly indicate that the carbon-oxygen scission leads to methane by a unimolecular homolytic decomposition reaction and that this reaction is accompanied by a bimolecular, hydrogen-abstraction-initiated pathway. There is no way that the relative rates of these processes can be predicted in coal matrices.

**Paraffinic Compounds.** Substances of this kind are constituents of subbituminous and bituminous coals. Their presence has been established by the examination of extracts,<sup>1</sup> by selective oxidation,<sup>6</sup> by controlled pyrolytic reactions,<sup>35</sup> and by the investigation of coal liquids.<sup>36</sup> These aliphatic substances usually occur as unbranched materials, some of which are chemically bonded and some of which are physically entrapped in the coal matrix.<sup>37</sup> At about the same time that Solomon proposed that the paraffinic constituents of coals were in part responsible for the formation of methane,<sup>14</sup> Calkins and his associates pointed out that the yield of methane that was obtained in the flash vacuum pyrolysis of coal was not closely related to the methylene group content of the coal.<sup>15</sup> While the literature on the thermal decomposition of the alkanes is extensive and the general patterns of reactivity have been worked out in some detail,<sup>38-40</sup> it is difficult to predict the chemistry of such materials in the coal matrix. Accordingly, we used *O*-alkylation to anchor pentadecyl, octadecyl, and octadecyl-*d*<sub>37</sub> fragments into the coal. The results for the *O*-octadecyl-*d*<sub>37</sub> fragment are displayed in Table II for convenient inspection.

The introduction of aliphatic material of any kind increases the yield of the low molecular weight hydrocarbons. As expected then, the yield of methane is enhanced by the incorporation of the highly paraffinic alkyl groups into the coal. However, the absence of methane-*d*<sub>2</sub> and methane-*d*<sub>3</sub> from the products revealed that the carbon atom of the methane did not originate from the added alkyl group. In contrast, yields of multiply labeled ethene, propene, and butadiene increased significantly. These observations support Calkins's contention<sup>15</sup> that the paraffinic constituents are not primarily responsible for the formation of methane.

These *O*-alkyl derivatives provide a realistic portrayal of the behavior of the paraffinic constituents in coal because the products that are obtained from the alkyl groups arise from two reaction channels that are com-

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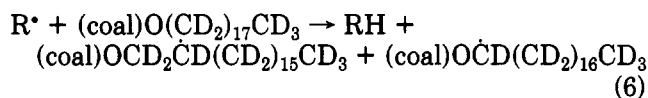
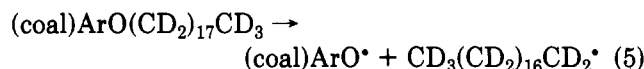
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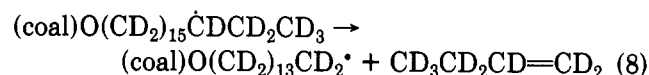
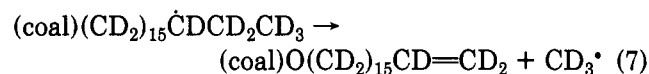
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mon for the ethers and the paraffins. One channel involves the elementary homolytic fission of the carbon-oxygen bond, eq 5, and the other channel involves deuterium atom abstraction reactions either at the benzyl position or at one of the other 16 secondary positions, eq 6.



The principal gaseous reaction products of the paraffins are low molecular weight alkenes that, presumably, are formed via familiar  $\beta$ -scission reactions of the intermediates shown in the equations. These radicals play a pivotal role in the decomposition of the alkyl fragments in coal.

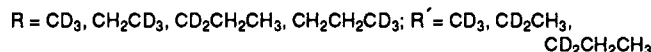
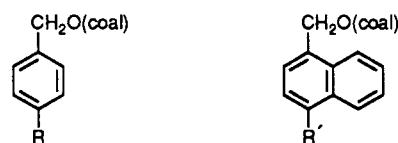
It seems unnecessary to reiterate the well-known tenets of elementary hydrocarbon radical chemistry,<sup>38-40,42-44</sup> but it is pertinent to note that the fragmentation reactions that could lead to methyl- $d_3$  radicals are statistically and energetically disfavored processes. Specifically, the secondary radical that is required in the formation of methyl- $d_3$  is formed in no more than 5% of the abstraction reactions. Once formed, the radical has three other reaction pathways, one of which is illustrated in eq 7, that are more favorable than the reaction, eq 8, that produces methyl- $d_3$ . Thus, it is not surprising that the paraffins provide only low yields of methane.



**Ipsso Dealkylation of Arylalkanes.** Previous investigations of pure arylalkanes have shown that dealkylation reactions occur at high temperature. In a classic study, Amano and associates showed that, in the presence of excess dihydrogen at temperatures near 500 °C, a hydrogen atom adds to the ipso carbon atom of toluene to form a methylcyclohexadienyl radical, which subsequently undergoes unimolecular decomposition to yield benzene and methyl radical.<sup>43</sup> Although the product distribution depends upon the reaction temperature and the dihydrogen pressure, demethylation, deethylation, and debenzylation can be experimentally observed.<sup>43-45</sup>

Some dealkylation reactions, for example, the demethylation of toluene under the conditions studied by Amano and co-workers, occur via ipso substitution re-

actions while others, for example, the deethylation of ethylbenzene, occur by hydrogen atom abstraction reactions followed by  $\beta$ -scission. Inasmuch as it has not been determined whether the reaction channels observed for pure molecules in well-controlled environments are important in the environment of rapidly degrading coal molecules, we undertook a study of the pyrolytic dealkylation of alkylphenyl and alkyl-naphthyl derivatives. Illinois No. 6 coal was modified by the introduction of labeled (3- and 4-alkylphenyl)methyl



and (4-alkylnaphthyl)methyl fragments. The methane- $d$ /methane ratio indicated that the methyl- $d_3$  groups in methylphenyl and methylnaphthyl coals were effective hydrogen donors. These observations are hardly surprising, but we were quite surprised by the fact that neither methane- $d_3$  nor methane- $d_2$  was obtained from the 3-(methyl- $d_3$ )phenyl, 4-(methyl- $d_3$ )phenyl, or 4-(methyl- $d_3$ )naphthyl derivatives in detectable amounts. For example, the pyrolysis of *O*-1-[4-(methyl- $d_3$ )phenyl]methyl coal at 788 °C provides 86% methane and 14% methane- $d$  but no detectable quantity of methane- $d_2$  or methane- $d_3$ . Thus, the methyl- $d_3$  fragment is an active participant in the pyrolysis, but dealkylation does not occur.<sup>48</sup>

The observation that demethylation is a minor pathway in the decomposition of the methylphenyl and methylnaphthyl derivatives of the Illinois coals prompted the investigation of samples with ethyl and propyl groups including *O*-1-[4-(ethyl-2,2,2- $d_3$ )phenyl]- and *O*-1-[4-(propyl-3,3,3- $d_3$ )phenyl]methyl coal.

The ethyl-2,2,2- $d_3$  group underwent exchange as expected to provide methane- $d$ , propane- $d$ , and propene- $d$  in the same relative abundance as the methyl- $d_3$  group and provided significant quantities of ethane- $d_2$ , ethane- $d_3$ , and ethene- $d_2$ . Specifically, *O*-1-[4-(methyl- $d_3$ )phenyl]methyl coal yielded approximately 2% ethane- $d_2$  and ethene- $d_2$ . In contrast, the pyrolysis of *O*-1-[4-(ethyl-2,2,2- $d_3$ )phenyl]methyl coal gives between 8 and 10% ethane- $d_2$ , ethene- $d$ , and ethene- $d_3$ . The formation of these labeled ethanes and ethenes established that deethylation occurs.

The deuterium atoms in the benzylic position are readily exchangeable, and this side reaction complicates the analyses of the results from the pyrolyses of *O*-1-[4-(propyl-1,1- $d_2$ )phenyl]methyl coal. This complication notwithstanding, significant amounts of the three-carbon-atom compounds were doubly labeled, indicating that depropylation occurs. The *O*-1-[4-(propyl-3,3,3- $d_3$ )phenyl]methyl coal provided even more substantial yields of the heavily labeled propanes than the coal with the 4-propyl-1,1- $d_2$  group.

The ethyl fragments contribute deuterium to the simple hydrocarbon gases. Approximately 1.6 deuterium atoms of the 6.0 deuterium atoms in the structure

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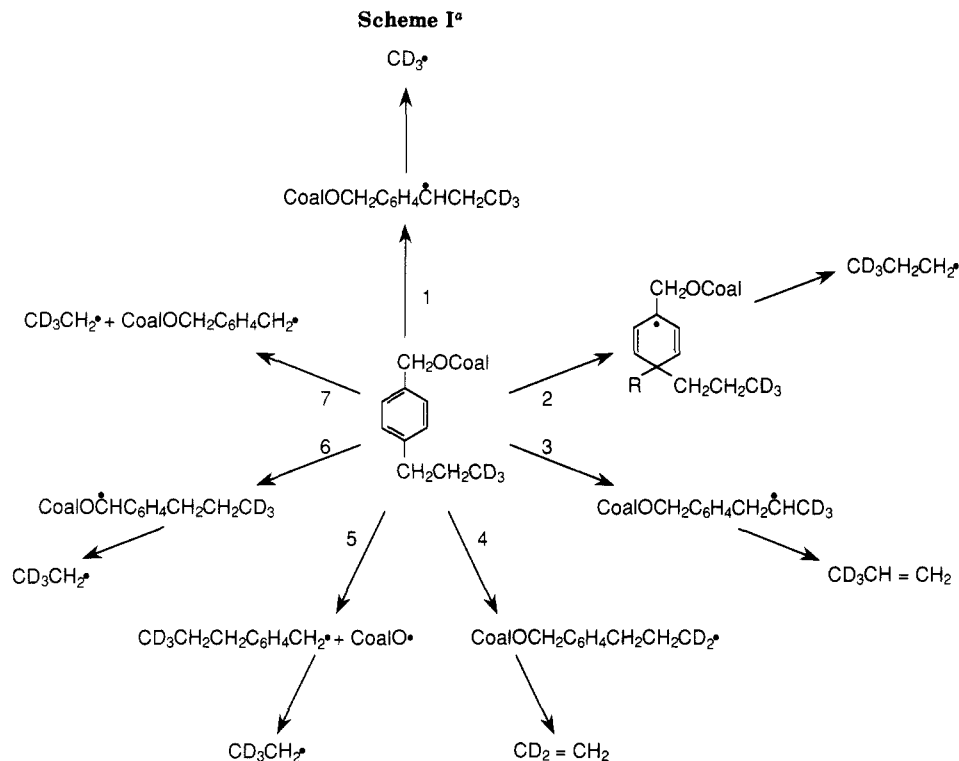
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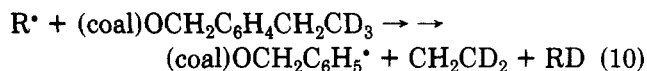
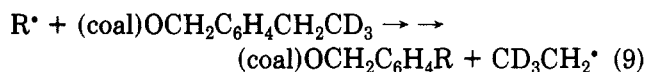
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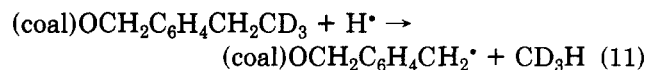
<sup>a</sup>Propyl group fragmentation pathways provide methane (37%) via 1 and (2), ethane (10%) via 1 and (5 and 6), ethene (32%) via 4 and (2, 5, 6, and 7), propane (2%) via 2, and propene (2%) via 2 and 3. The reaction channels that are mentioned in parentheses are less important ones.

are transferred under the reaction conditions. Dealkylation occurs to a much smaller extent. Comparable results were obtained from the propyl- $d_3$  fragment. In this case, approximately 3.1 deuterium atoms of the 8.0 deuterium atoms in the structure are transferred in abstraction reactions. Dealkylation to yield propane and propene accounts for about 4% of the labeled propyl groups in this sample.<sup>48</sup>

Dealkylation can be accomplished in several ways, including ipso substitution, eq 9, or abstraction followed by  $\beta$ -scission, eq 10.



The results for the ethyl-2,2,2- $d_3$  derivative establish that ipso deethylation contributes to the production of ethane. Some very direct lines of evidence are available, but the fact that ethane- $d_3$  is formed in significant amounts from the ethyl- $d_3$  derivative is especially pertinent. This compound cannot be produced in abundance except via direct displacement or ipso substitution. Other results allow us to discount the direct displacement pathway. Specifically, we did not observe the formation of methane- $d_3$  in an energetically more favorable case, eq 11.



The results for the phenyl derivatives with propyl-1,1- $d_2$  and propyl-3,3,3- $d_3$  groups are more difficult to interpret because the ipso substitution and abstraction reaction pathways give the same multiply labeled products and because exchange reactions adversely in-

fluence the interpretation of the data for the doubly labeled compound. However, the observations are consistent with 9% ipso depropylation.

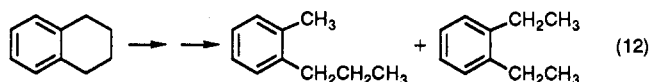
The energy requirements for ipso dealkylation are significant because the delocalization energy of the aromatic compound is disrupted. To gauge the impact of this factor on the pyrolytic reactions, we studied *O*-1-[4-(ethyl-1,1- $d_2$ )naphthyl]- and *O*-1-[4-propyl-1,1- $d_2$ )naphthyl]methyl coal. The data indicate that the ethyl and propyl groups are cleaved from the naphthalene ring at about the same rate as for the benzene derivatives.

**Other Methane Sources.** Alkanes and alkenes are formed from the ethyl and propyl fragments in several ways in addition to ipso dealkylation. The attention given to the pathways for the formation of methane, ethane and ethene, and propane and propene from labeled ethyl- and propylaryl fragments proved fruitful.<sup>48</sup> The very rich chemistry of the propylaryl fragment is displayed in Scheme I.

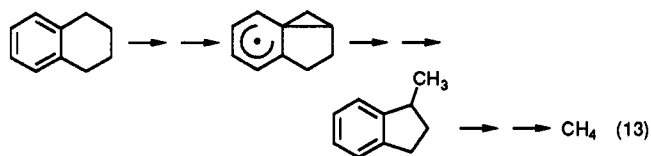
The homolysis of the carbon-oxygen bond in (4-propylphenyl)methyl coal, reaction 5, is a prominent process that accounts for about 30% of the benzylic groups that were introduced into the coal. This homolytic cleavage followed by remote  $\beta$  carbon-carbon scission, reaction 5, may contribute to the yield of ethane- $d_3$ , but no definite evidence for this kind of fragmentation or for other vinylogous  $\beta$ -scission processes such as reaction 6 has been obtained in our studies. They are included in Scheme I for completeness.

Approximately 80% of the *O*-propylbenzyl groups that remain in the solid experience hydrogen atom abstraction followed by  $\beta$ -scission to form gaseous hydrocarbons, reactions 1, 3, and 4. The relatively facile conversions of the simple alkyl groups into methane,

ethane, and ethene imply that these kinds of reactions can play a significant role in the conversion of coal macromolecules into gaseous hydrocarbons, but it is notable that few pendant ethyl (0.25 mol/100 mol of C) or propyl (0.05 mol/100 mol of C) groups exist in bituminous coals.<sup>49</sup> Consequently, if such fragments are involved in the formation of gaseous hydrocarbons, rather deep-seated transformations of the coal structure must be postulated. The connection between the observed chemistry of the ethyl and propyl groups and coal structures can be realized through the relatively abundant hydroaromatic structures with five- and six-membered aliphatic rings, eq 12. We prepared a



modified coal that contained *O*-2-[5,6,7,8-tetrahydronaphthyl-5-<sup>13</sup>C]methyl and *O*-2-[5,6,7,8-tetrahydronaphthyl-8-<sup>13</sup>C]methyl groups and another sample that contained *O*-2-[5,6,7,8-tetrahydronaphthyl-6-<sup>13</sup>C]methyl and *O*-2-[5,6,7,8-tetrahydronaphthyl-7-<sup>13</sup>C]methyl groups and subjected these two coals to pyrolysis.<sup>50</sup> Although the results were somewhat imprecise, about 6% of the tetralyl fragments with the label in the 5- or 8-position were converted to methane-<sup>13</sup>C at 750 °C. In contrast, the corresponding coal with the <sup>13</sup>C label in the 6- or 7-position did not yield a detectable quantity of methane-<sup>13</sup>C. These findings are inconsistent with explanations based upon the homolytic ring cleavage reactions but favor an interpretation based upon ring contraction and demethylation, eq 13.<sup>51-53</sup> Judging



from the distributions of compounds in coal extracts and liquefaction products,<sup>54</sup> peri-fused aromatic and hydroaromatic compounds are considerably more abundant than the kata-fused derivatives. In view of the rates at which hydrogen-atom transfers occur under the pyrolytic conditions, we infer that the hydrogenation-dehydrogenation and ring contraction-demethylation processes are significant for methane formation. Demethylation almost certainly also occurs during the accompanying cyclization and aromatization reactions

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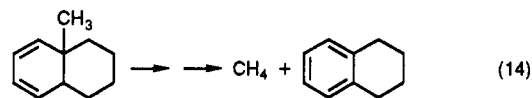
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as illustrated in eq 14 for the demethylation of a hydroaromatic compound with a fragile bridgehead methyl group.



## Conclusion

In summary, the work of Juntgen, Suuberg, Solomon, and others presents a unifying view of the kinetic patterns for the decomposition of coal and offers insight concerning the sources and yields of the various gaseous products formed during coal pyrolysis.<sup>10-15,26,55</sup> The establishment of the relationship between the constitution of the coal and the ultimate product distribution realized in pyrolysis has been a common goal. The recent investigations provide new information on the probable pathways for the formation of gaseous products during the coal pyrolysis in the absence of added dihydrogen. Bond homolysis and hydrogenation abstraction reactions as well as bimolecular hydrogen-transfer processes appear to be the principal initiation reactions. No single reaction sequence appears to play a unique and dominant role in the formation of the simple gaseous hydrocarbons that are produced in pyrolysis. Nevertheless, it is clear that methoxy groups under demethylation; such reactions are certainly important for methane formation from lignites and sub-bituminous coals, but insignificant in the case of bituminous coals which do not have substituents of this kind. Paraffinic elements preferentially yield two- and three-carbon-atom derivatives rather than methane. The relatively abundant aromatic methyl groups do not appear to be prominent methane producers. Rather, somewhat more complex reaction networks which involve hydrogen transfer reactions that interconvert aromatic and hydroaromatic compounds and lead to opportunities for demethylation from benzylic positions and reactive aliphatic positions need to be considered in the development of an overall scheme for coal pyrolysis. Finally, it should be mentioned that pericyclic processes including ene reactions and cycloaddition reactions as well as hydrogen transfers also doubtless contribute in subtle ways to determine the outcome of pyrolytic chemistry. At the present, however, the evidence requires analysis of the results on the basis of a myriad of radical processes.

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