

COAL ALKYLATION AND PYROLYSIS

Leon M. Stock

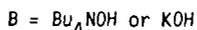
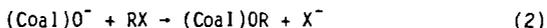
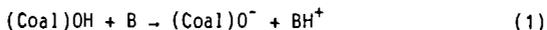
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INTRODUCTION

Investigations employing alkylation, reductive alkylation, and related kinds of chemical transformations have provided new information concerning the structural characteristics of representative bituminous coals (1). The nature of the oxygen functional groups in coals are of rather special interest because they strongly influence the reactions of the coal. Accordingly, we determined the relative abundance these groups during a study of the alkylation and reductive alkylation of Illinois No. 6 coal (2). The availability of information of this kind, especially the hydroxyl group content, led us to consider a new approach for the evaluation of the factors governing the reactions of coal molecules. Specifically, knowledge of the hydroxyl group distribution provided an opportunity to introduce new organic groups into coal at selected, known locations. Once alkylated, the modified coals could be investigated in a variety of ways to gain more information on their structure and reactivity. The presentations of G.R. Dyrkacz (3) and K.W. Zilm (4) illustrate some aspects of this activity. We, in collaboration with R.F. Zabransky of the Institute of Gas Technology, have examined the pyrolytic reactions of the modified coals.

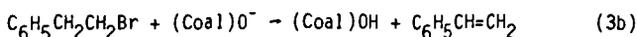
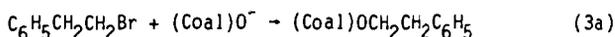
RESULTS AND DISCUSSION

Preparation. At first, we contemplated using reductively alkylated coals in studies of liquefaction and gasification. Work with such kinds of modified coals is attractive because the reductively alkylated materials are significantly soluble in ordinary organic solvents. However, the achievement of solubility is realized at the cost of carbon-carbon bond cleavage reactions, as well as extensive O- and C-alkylation reactions (1). It appeared that the reactivity patterns of these modified coals might not be entirely representative of the original coals. Therefore, we elected to use simple alkylation procedures to modify the coals. The O-alkylation reaction worked out by R. Liotta and his associates (5) proved very suitable for our requirements. Illinois No. 6 coal and other coals can be very selectively alkylated using this reaction scheme, equations (1) and (2).



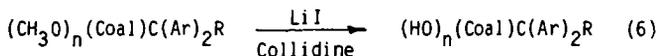
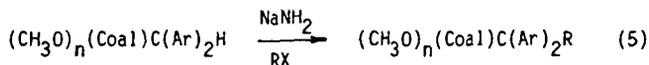
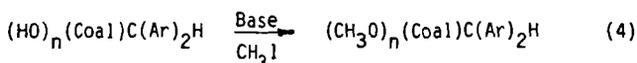
R = Primary alkyl halide or tosylate

In the course of the study, it became clear that tetrabutylammonium ions could be tenaciously retained in the modified coals and could produce unwanted by-products during the pyrolytic reactions. Potassium hydroxide was used to circumvent this problem. Certain primary alkyl halides, for example, the 2-phenylethyl bromides, selectively undergo elimination reactions rather than etherification reactions, equation (3). This difficulty was avoided by the



substitution of alkyl tosylates for alkyl bromides (6).

C-Alkylation was accomplished as outlined in equations (4) to (6).



Using techniques of this kind, we prepared many modified coals including derivatives with simple alkyl and allyl groups, arylmethyl and aryethyl fragments and compounds with aromatic and hydroaromatic structures, for example 9,10-dihydrophenanthrene. In order to trace the chemistry, H-2 and C-13 labels were introduced into the modified coals. Space limitations do not permit a discussion of the methods employed for the preparation and characterization of these compounds, but it should be noted that infrared and magnetic resonance spectroscopy as well as elemental analyses have been used extensively to establish their structures.

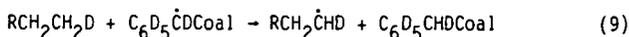
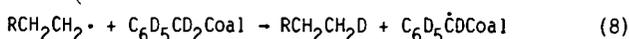
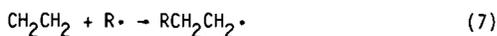
Pyrolysis. The pyrolysis experiments were carried out on a wire screen in a reactor of the type described by Anthony and his coworkers (7). In a typical experiment, 10-15 mg of coal was placed on a preconditioned 325 mesh, 316 stainless steel screen. The reactor was flushed with high-purity helium. Then, the pressure in the reactor was adjusted to 0.12 MPa and the sample was heated at $1000^\circ\text{C s}^{-1}$ to the desired final temperature usually between 600 and 850°C . After the reaction system had cooled, the gaseous products were absorbed on a Tenax column. The reaction vessel was then opened and the char and tar yields were determined gravimetrically.

The Tenax column containing the gaseous products was heated to transfer the absorbed materials to a calibrated vessel. The volatile products were analyzed using a Finnigan Model 4510 GC-MS system. The material balances in

these experiments were very good.

The isotopic composition of the gaseous products was also determined by GC-MS analysis. The procedures for the analyses of the labeled products were developed on the basis of the study of pure labeled compounds.

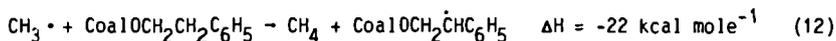
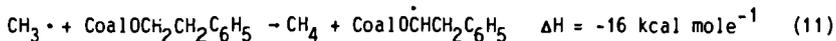
Methylated and Benzylated Coals, A Perspective of Pyrolysis.--The study of the O-methyl and O-benzyl coals established several pertinent points (8-10). First, the modified coals are more reactive than the unmodified starting materials. This enhanced reactivity is particularly evident in the increased yields of carbon monoxide and methane. The enhanced yields of these materials suggests that the increased radical density resulting from the modification of the coal promotes other secondary radical reactions that lead to demethylation or decarbonylation. Hence, the results strongly imply that the extent of small-fragment molecule formation depends in a direct way upon the concentration of radicals within the coal particles. The enhancement of the production of methane may, in part, be attributed to the increased concentration of effective hydrogen donor groups which terminate reactions that would otherwise lead to undesirable char-forming reactions. Second, the exchange patterns strongly suggest that many reactions occur reversibly and that radical addition reactions compete favorably with fragmentation and substitution reactions. Deuterium-labeled ethene, propene and butenes are formed during the rapid pyrolyses of the O- and C-benzyl-d₇ coals. Similar, significant amounts of deuterium are incorporated in the ethene produced from each coal. It seems unlikely that ethene is produced by the dehydrogenation of ethane under the experimental conditions. The most plausible pathways for the formation of ethene-d involve exchange reactions prior to the formation of ethene via pericyclic processes, β-scission reactions, and rapid addition-elimination reactions. These formulations all require that the primary reactive products formed in the original decomposition reactions undergo secondary reactions within the small coal particles, even in this reaction system where the secondary reactions of the initial products are minimized.



Third, the non-random distribution of the isotopic labels in the products, for example, the selective abstraction of hydrogen from the benzylic ether, indicates that the reactions within the coal particle are kinetically controlled even at temperatures near 850°C.

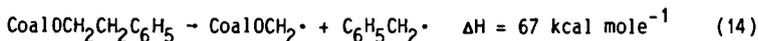
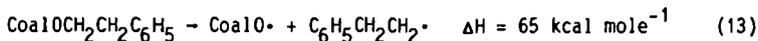
Phenylethylated Coals, The Origins of Ethene.--Next, we turned our attention to the reactivity of O-2-phenylethyl coals. The results can fruitfully be discussed on the basis of the calculated energy requirements (11) for several key reactions. The hydrogen atom abstraction reactions of the 2-phenyl-

ethyl fragment by alkyl radicals, equations (11) and (12), are thermochemically very favorable.

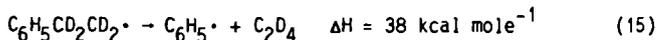


The yields of the simple gaseous paraffins are enhanced and these materials are extensively labeled when 0-2-phenylethyl- d_2 and - d_4 derivatives are used. These observations may be attributed to the occurrence of reactions (11) and (12). Moreover, it is evident that the transient alkyl radicals abstract hydrogen atoms from both the 1 and 2 positions of the 0-(2-phenylethyl) fragment. The methane-d/methane ratios 0.05, 0.09, and 0.17 for the 1,1- d_2 , 2,2- d_2 , and 1,1,2,2- d_4 compounds imply that hydrogen (deuterium) is selectively abstracted from the 2 position of the 2-phenylethyl fragment. This observation is in accord with the differences in bond energies noted in equations (11) and (12).

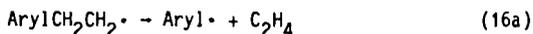
The predominant homolytic fragmentation pathways through which radicals could be formed from the 2-phenylethyl groups are shown in equations (13) and (14).

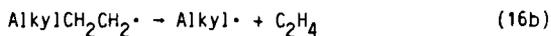


The results for labeled compounds establish that such reactions play a role. Specifically, the formation of significant amounts of toluene- d_2 from the 0-(2-phenylethyl-2,2- d_2) and 0-(2-phenylethyl-1,1,2,2- d_4) derivatives clearly indicates the involvement of benzyl-1,1- d_2 radical in the reaction sequence. In addition, labeled ethylbenzenes are found among the reaction products. Indeed, 2-phenylethane-1,1,2,2- d_4 is the most abundant form of 2-phenylethane. Ethene- d_3 and ethene- d_4 are prominent products of the thermal decomposition of the 0-2-phenylethyl-1,1,2,2- d_4 coal. We postulate that 2-phenylethyl radical undergoes fragmentation to yield ethene and phenyl radical, equation (15).



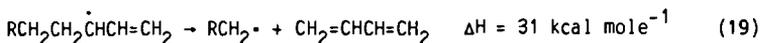
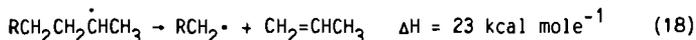
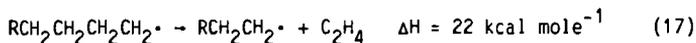
Although endothermic, this reaction apparently occurs readily under the experimental conditions. This observation provides strong support for the view that dealkylation reactions, equations (15) and (16), play a prominent role in ethene formation.



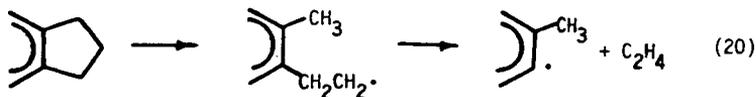


Our results provide strong support for the suggestions of Calkins and his co-workers who pointed out that there was a relationship between the yields of ethene, propene, and butadiene obtained in flash pyrolysis and the quantity of paraffinic hydrocarbons in the coal and proposed that such substances were the precursors of the low molecular weight hydrocarbons (12,13).

It seems reasonable to postulate that ethene, propene, and butadiene are produced from long chain alkyl radicals, equations (17) to (19)



Ethene and propene are also obtained from hydroaromatic constituents, equation (20). The high energy requirements notwithstanding, the available evidence

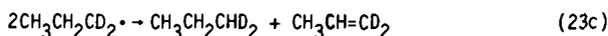
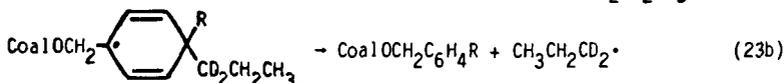
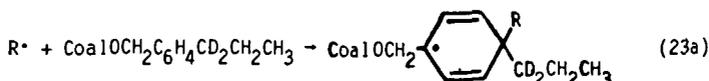
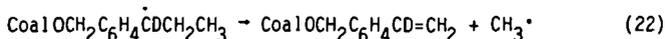
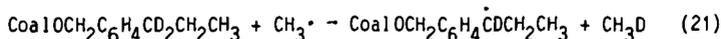


points to the importance of β -scission reactions of 2-arylethyl and 3-aryl-2-propyl radicals and their derivatives for the production of ethene, propene and related substances.

(4-Propylphenyl)methylated Coals. Ipso Replacement.--Ipso substitution reactions also occur. Vernon and his associates showed that such reactions were important for the dealkylation of aryl alkanes under the conditions of coal liquefaction reactions (14). This feature of the chemistry was confirmed by examination of the reactions of labeled and unlabeled 4-propylben-

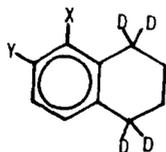


zene derivatives. These compounds provide rather high yields of C₂ and C₃ hydrocarbons. Indeed, the yield of ethane and ethene triples and the yield of propane and propene doubles when these fragments are present in coal. Even more significant, very large quantities of propane-d₂ are formed from the labeled derivative. In brief, the side-chain fragments are good hydrogen donors, equation (21), and undergo demethylation, equation (22). Ipso substitution chemistry accounts for the high yields of propane-d₂ and propene-d₂, equation (23).



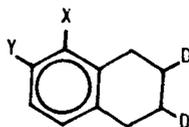
Tetralin Derivatives, Pericyclic Processes.--Our most recent studies have focused on the role of pericyclic processes in the thermal decomposition reactions of coals. Although there is ample evidence that such kinds of reactions occur readily under the conditions employed for the pyrolysis of coal, most workers in the field with the notable exception of Virk and his group (15) have adopted the view that coal decomposition is, with the exception of water-forming reactions, a free radical process (16). Although the early searches for pericyclic reactions during the thermal decomposition of coal have not been successful (17,18), we reconsidered the issue because the energy requirements for many pericyclic reactions are known to be modest.

Illinois No. 6 coal samples modified with labeled tetralin fragments, 5- and 6-(1,2,3,4-tetrahydronaphthyl-1,1,4,4-d₄)methyl bromide and 5- and 6-(1,2,3,4-tetrahydronaphthyl-2,3-d₂)methyl bromide, were pyrolyzed to determine



X = CoalO, Y = H

X = H, Y = CoalO



X = CoalO, Y = H

X = H, Y = CoalO

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