

CATALYTIC DEHYDROGENATION OF COAL III. HYDROGEN EVOLUTION AS A FUNCTION OF RANK*

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Dehydrogenation of coal using a one percent palladium on calcium carbonate catalyst in the presence of phenanthridine as solvent gives almost pure hydrogen gas as the product. The rank of coal affects the yield of hydrogen from the corresponding vitrain; for coals ranging from high volatile C bituminous to anthracite, the hydrogen evolution decreases gradually with increasing rank of coal; lignites and subbituminous coals give less hydrogen than do low rank bituminous coals. For bituminous coals, the hydrogen evolution (atoms of hydrogen evolved per 100 carbon atoms in the coal) is a linear function of the atomic H/C ratio and also of the atomic O/C ratio. Lignites and subbituminous coals fall outside of the lines defining the bituminous coals. Some ideas on the process of coalification are presented: it is suggested that lignites and subbituminous coals contain some cyclic carbon structures which are neither aromatic nor hydroaromatic; that low rank bituminous coals contain large amounts of hydroaromatic structures; and that higher rank bituminous coals contain increasing amounts of aromatic structures.

INTRODUCTION

The vast literature on chemical reactions of coal^{1,2} contains (until quite recently) very few references to any work on dehydrogenation. This may be due in part to the paucity of systematic studies on the dehydrogenation of organic compounds under conditions which might be expected to cause relatively little disruption of the coal structure; i.e., dehydrogenation in the liquid phase[†] at temperatures below 400°C. The dehydrogenation reagents usually used for pure compounds are metallic catalysts³, sulfur³, selenium³, and quinones^{3,4}. The dehydrogenation of coal by sulfur⁵ has received considerable attention; the hydrogen removed from the coal is evolved as hydrogen sulfide. Selenium has not, to our knowledge, been used with coal; because of the higher temperature required and the poor yields usually obtained, selenium seldom offers any advantage over sulfur³; in a selenium dehydrogenation, the hydrogen removed is evolved as hydrogen selenide. Benzoquinone with coal has been investigated⁶; the reaction is a hydrogen transfer⁴, giving hydroquinone, and the results are difficult to interpret⁷. Iodine as a dehydrogenation agent has also been studied with coal⁸; the hydrogen removed from the coal is evolved as hydrogen iodide. Again, the results are not easy to evaluate; the temperature of reaction is high; and there is very little work on organic compounds which can serve as a basis for comparison^{9,10}. Bromine, one of the oldest dehydrogenation reagents³, has been of little value¹.

The first use of a metallic catalyst for the dehydrogenation of coal was reported by the present authors¹¹; the reaction was conducted in the presence of a solvent (vehicle), and almost pure hydrogen gas was evolved. The reversibility of the reduction and dehydrogenation of coal has also been investigated¹². In this paper we wish to summarize the development of the method, the experimental

*For the preceding papers in this series, see references 11 and 12.

† For an excellent and up to date review see ref. 3.

procedure, and, most important, the effect of the rank of the coal upon the amount of hydrogen formed. The purpose of these studies is twofold: first, to obtain information which may give some insight into the structure of coal; second, to obtain large amounts of hydrogen from coal. It is hoped that development of cheaper solvents and catalysts might enable hydrogen to be produced economically; the coal residue could then be burned for fuel.

EXPERIMENTAL

Preliminary experiments in which coal, catalyst, and vehicle were refluxed showed that the hydrogen evolution was influenced by reflux rate, heating rate, bath temperature, and depth of immersion of the reaction flask into the bath. Accordingly, the previous apparatus used a stirrer and a heating mantle^{11,12}. A Hershberg tantalum wire stirrer with a glass bearing lubricated with silicone grease was used; later, a magnetic stirrer was found to be more convenient, to give superior results, and to obviate crust problems (see below). When the Hershberg stirrer was used, the reactants (0.500 g of dried, -200 mesh coal, 0.550 g of catalyst, and 7.50 g of the vehicle) were weighed into a 50 ml two-neck flask. The charge was mixed thoroughly with a spatula. The flask was then fitted with the stirrer and with an adapter which included both a dip-tube to serve as a thermocouple well and a side arm which was attached to a 250 ml gas buret. Provision was made for admission of helium to the system and for sampling the evolved gas after the reaction. The apparatus was thoroughly flushed with helium and pressure-tested for leaks. Flushing consisted essentially of admitting helium to the system, expelling the gas, adding fresh helium, and repeating this procedure three to five times. As a check upon the efficacy of flushing, the last expelled flush can be sampled; it should contain at least 99 percent helium (all gases were analyzed by mass spectrometry). The charge was then vigorously refluxed (heating mantle) with stirring for 5.0 h, preceded by a carefully standardized 0.5-h period of heating up to temperature. The reduced 1 percent palladium on calcium carbonate catalyst was prepared by Engelhard Industries, Inc., Newark, N. J. The same batch of catalyst was used in all of the runs described here, with the exceptions noted below. (See Discussion.) The catalyst was dried at 60°C and 1 mm; coals were dried to constant weight at 100° and 1 mm.

This experimental procedure was effective, but it was not convenient, and the stirrer sometimes jammed in the bearing, requiring repetition of a run. Also, some catalysts were found to convert the coal to a hard, brittle, insoluble crust after only a short heating period; this gave low and erratic values for hydrogen. (Crust formation could sometimes be avoided by very slow and prolonged heating to reflux.) It was found that magnetic stirring circumvented these problems and was also much more convenient. A 35 ml one-neck flask heated by an electric mantle was used. A pyrex-enclosed alnico stirring bar, 7/8 in. long, was placed in the flask. An alnico horseshoe magnet (ca. 50 pound pull) was located below the mantle and rotated by an ordinary stirring motor. The rest of the apparatus was as described above. With this modification, stirring was much more vigorous and crust formation usually did not take place. If in any run a solid crust began to form on the surface of the boiling liquid or on the walls of the flask, stirring was stopped and a small alnico magnet was brought near a point on the side of the flask; this pulled the stirring bar away from the large magnet, and the bar was moved around to break the crust. The small magnet was then removed, and stirring resumed with the large magnet. A few repetitions of this broke up any crust.

For most coals, the bulk of the gas was evolved during the first two hours of reflux, but gas evolution was still continuing at a slow rate (ca. 4 or 5 ml in 30 min) after 5 h. At the end of the reaction period, the gas volume was measured and the gas then thoroughly mixed and sampled. A typical analysis (helium-free basis) for the gas from an hvab coal is 96.4 percent H₂, 0.5 percent N₂, 0.4 percent CH₄, 0.1 percent ethylene, 0.6 percent CO, 0.1 percent ethane, 1.5 percent CO₂, and small amounts (0.1 percent) of other alkanes and alkenes. Lower rank coals gave larger amounts of CO, CO₂, and CH₄. Only the molecular hydrogen itself was considered to be hydrogen evolved; hydrogen in hydrocarbons was disregarded. In the calculations, it was assumed that the gas was saturated with water vapor. In all instances, blank runs (vehicle and catalyst, no coal) were made and corrections applied. The blanks were found to be a function of both the vehicle and the catalyst; two different batches of the same catalyst would give slightly different blanks. Coal-vehicle blanks (without catalyst) were found to be negligible and were disregarded. As would be expected, inadequate flushing of the apparatus led to low hydrogen values. It was also found that slight air oxidation of vitrains resulted in low hydrogen values; it is desirable to use a sample within a period of two weeks of grinding.

We thank D. E. Wolfson for obtaining many of the coal samples used. We are very grateful to B. C. Parks, Pittsburgh Mining Research Center, Bureau of Mines, who prepared the hand picked vitrain samples.

DISCUSSION

In the preliminary development of the method, some experiments were done on the dehydrogenation of 1,2,3,4,5,6,7,8-octahydrophenanthrene, using a 5 percent rhodium on alumina catalyst and refluxing *o*-terphenyl (bp 332°C) as a vehicle. No stirring was used. With a bath temperature of 300°-350°C for 1 h, about 98-99 percent of the theoretical amount of hydrogen gas was obtained, but the hydrogen evolution was never quite 100 percent. No formation of triphenylene (by cyclo-dehydrogenation of *o*-terphenyl) could be detected. In one experiment octahydrophenanthrene was dehydrogenated in the presence of about 5 percent by weight of dibenzothiophene (no vehicle); the hydrogen evolution was high (in addition, some hydrogen probably was used to cleave carbon-sulfur bonds) and the yield of phenanthrene was over 95 percent. It is thus apparent that the sulfur in coal should not poison the dehydrogenation catalyst. This is in accord with several reports on the dehydrogenation of partially reduced heterocyclic sulfur¹⁰, oxygen¹³, and nitrogen¹⁴⁻¹⁷ compounds, in good yield, with little cleavage of the carbon-hetero atom bond; for example, 1,2,3,4-tetrahydridibenzothiophene is converted to dibenzothiophene by palladium on carbon in 80 to 94 percent yield¹⁰.

Experiments were then done on dehydrogenation of vitrain from Bruceton coal (hvab, Pittsburgh Bed, Bruceton, Allegheny County, Pa.) with various catalysts. Vitrain refluxed (without stirring) 2 h with *o*-terphenyl and 30 percent palladium on calcium carbonate gave off about 7.3 percent of the hydrogen in the vitrain as hydrogen gas; a pyridine-soluble extract of Bruceton vitrain under the same conditions gave 9.0 percent of its hydrogen; the pyridine soluble extract with phenanthridine as vehicle and 30 percent palladium on calcium carbonate gave 13.7 percent hydrogen in 2 h reflux and 30 percent hydrogen in 7 h. Bruceton vitrain with 30 percent palladium on carbon heated at 377° to 402°C (no vehicle) gave 0.2 percent hydrogen. Bruceton vitrain refluxed with *o*-terphenyl and various palladium, ruthenium, and rhodium catalysts gave 3 to 7 percent hydrogen. Bruceton vitrain refluxed 2 h with *o*-terphenyl and a molybdenum sulfide or tungsten sulfide catalyst gave both hydrogen (about 2 percent) and hydrogen sulfide; these results did not seem promising and no further work was done with sulfide catalysts.

All of the experiments discussed above were done with a refluxing system but no stirrer. Attention then turned to the development of an apparatus which could be stirred. Our previously published work^{11,12} was done using the Hershberg stirrer. The remainder of the work discussed in this paper used the magnetic stirrer (see Experimental), and is concerned with the effect of the rank of the coal upon the hydrogen evolved from the corresponding vitrain. It should be pointed out that comparison of the present results with previous data showed that, for most vitrains, magnetic stirring gave significantly greater yields of hydrogen than did the Hershberg stirrer. It seems probable that even with those vitrains and catalysts which have little tendency to form crusts with the Hershberg stirrer, an insolubilization reaction (polymerization, cross-linking, etc.) takes place during dehydrogenation which results in the coal being made too insoluble in the vehicle to react further, after partial but not complete dehydrogenation. With the more efficient magnetic stirring, dehydrogenation goes at a more rapid rate and is completed before insolubilization can have much effect on the final hydrogen evolution. Some data substantiating this is given in table 4, which shows that for two representative vitrains (Harmattan and Pocahontas No. 3), which give more hydrogen with magnetic than with Hershberg stirring, the magnetically stirred run evolves gas at a faster rate. However, for Bruceton vitrain (the only vitrain giving essentially the same hydrogen value for both stirring methods) the rates of gas evolution are almost the same for both runs.

Table 1 gives the identity and source of 36 coals used in this work. Of these, cannel coal was taken with the thought that its high hydrogen content might lead to a large hydrogen evolution, a hope which did not materialize. Cannel coal was used as the whole coal. The two semianthracites were also whole coals; microscopic examination showed that the Western Middle Field contained over 90 percent vitrain; the Bernice Field was less than 25 percent vitrain. The other 33 coals were used in the form of hand-picked vitrains. Tables 2 and 3 give the ultimate analyses of the samples and the results of dehydrogenation. The results are expressed in three ways: percent of the total hydrogen in the coal which is evolved as hydrogen gas; atoms of hydrogen evolved per 100 carbon atoms in the starting material; and milliliters of hydrogen evolved per gram of starting material.* The last figure (ml/g) can be converted to cubic feet per ton by multiplying by 32.0. This would obviously be of interest in indicating in a very rough way the possible economic value of the process. The largest value obtained is for the vitrain from a Utah hvcb coal (Liberty mine) which gives 9380 cubic feet of H₂ gas per ton on a dry basis, or 9890 cubic feet per ton on a dry ash-free basis. The second figure (H/100 C atoms) is related to the hydroaromatic† structures in the starting coal (neglecting side reactions for the present); any completely reduced structure such as cyclohexane, decalin, or perhydrocoronene would give a value of 100 H/100 C. The first figure (percent H₂ evolved) is also related to the amount of hydroaromatic structure in the coal, but not in a simple and direct manner; it is, however, a convenient figure in that it expresses a yield of product.

*The first two of these are independent of ash content; the third is not, and is on an ash basis.

†The term hydroaromatic is used in the sense defined by Fieser and Fieser¹⁸. Hydro derivatives of aromatic compounds are called hydroaromatic. Alicyclic substances containing six-membered rings but having substituents that block conversion to the aromatic state unless they are eliminated (such as 1,1-dimethylcyclohexane or 9-methyldecalin) are not classified as hydroaromatic.

Table 1. Identity and source of samples used in dehydrogenation

Lignite, Beulah-Zap Bed, Zap Mine, North American Coal Co., Zap, Mercer County, North Dakota

Lignite, Kincade Mine, Burke County, North Dakota

Lignite, Beulah-Zap Bed, North Unit, Beulah Mine, Knife River Coal Mining Co., Beulah, Mercer County, North Dakota

Subbituminous, Roland-Smith Bed, Wyodak Strip Mine, Wyodak Coal and Manufacturing Co., Gillette, Campbell County, Wyoming

Subbituminous, Dietz Bed, Big Horn Mine, Sheridan County, Wyoming

Subbituminous, Laramie Seam, Washington Mine, Clayton Coal Co., Erie, Weld County, Colorado

Subbituminous, Pioneer Canon No. 1 Mine, W. D. Corley Co., Florence, Fremont County, Colorado

Subbituminous, Rock Springs No. 7, 7-1/2, 9, and 15 Coal Beds, Superior, Sweetwater County, Wyoming

High-volatile B bituminous, Illinois No. 6, Green Diamond Mine, Mid-Continent Coal Corp., Marissa, St. Clair County, Illinois

High-volatile B bituminous, Illinois No. 6 Seam, Mecco Mine, Atkinson, Henry County, Illinois

High-volatile C bituminous, No. 11 Coal Bed, Rainbow No. 7 Mine, Gunn-Quealy Coal Co., Quealy, Sweetwater County, Wyoming

High-volatile C bituminous, Illinois No. 7 Bed, Harmatten Mine, Vermillion County, Illinois

High-volatile C bituminous (possibly high-volatile B bituminous), Liberty Bed, Liberty Mine, Liberty Fuel Co., Helper, Carbon County, Utah

High-volatile B bituminous, Illinois No. 6 Bed, Orient No. 3 Mine, Freaman Coal Mining Corp., Waltonville, Jefferson County, Illinois

High-volatile B bituminous, Kentucky No. 9, Pleasant View Mines 9-11, Western Kentucky Coal Co., Madisonville, Hopkins County, Kentucky

High-volatile B bituminous, Kentucky No. 9, DeKoven Mine, Sturgis, Union County, Kentucky

High-volatile A bituminous, Pittsburgh Bed, Bruceton, Allegheny County, Pennsylvania

High-volatile A bituminous, Pond Creek Coal, Majestic Mine, Pike County, Kentucky

High-volatile A bituminous, Powellton Bed, Elk Creek No. 1 Mine, Logan County, West Virginia

High-volatile A bituminous, Eagle Bed, Kopperston Mine, Kopperston, Wyoming County, West Virginia

Medium-volatile bituminous, Sewell Bed, Lochgelley Mine, New River Coal Co., Lochgelley, Mt. Hope, Fayette County, West Virginia

Medium-volatile bituminous (possibly high-volatile A bituminous), Lower Freeport Bed, Coal Valley No. 7 Mine, Indiana County, Pennsylvania

Low-volatile bituminous, Lower Kittanning Bed, Melcroft Mine, Eastern Associated Coal Corp., Fayette County, Pennsylvania

Medium-volatile bituminous, Lower Banner, Buccaneer Mine, Patterson, Buchanan County, Virginia

Medium-volatile bituminous, Sewell Bed, Marianna Mine, Wyoming County, West Virginia

Low-volatile bituminous, Beckley Bed, Maben Mine, Raleigh County, West Virginia

Medium-volatile bituminous, Sewell Seam, Crab Orchard Mine, Winding Gulf Coals, Inc., Raleigh County, West Virginia

Low-volatile bituminous, Lower Hartshorne Bed, Garland Coal and Mining Co., Prospect opening, Arkoma Coal Basin, Le Flore County, Oklahoma

(Continued)

Low-volatile bituminous, Upper Kittanning Bed, Stineman No. 10 Mine, Johnstown, Cambria County, Pennsylvania
 Low-volatile bituminous, Pocahontas No. 4 Bed, McAlpine Mine, Winding Gulf Coals, Inc., McAlpine, Raleigh County, West Virginia
 Low-volatile bituminous, Lower Kittanning Bed, Toth Mine, Hooversville, Cambria County, Pennsylvania
 Low-volatile bituminous, Pocahontas No. 3 Bed, Buckeye No. 3 Mine, Page Coal and Coke Co., Stephenson, Wyoming County, West Virginia
 Semianthracite, Bernice Field, Buckwheat No. 1 Mine, E and B Coal Co., Mildred, Sullivan County, Pennsylvania
 Semianthracite, Western Middle Field, Buckwheat No. 5 Mine, Trevorton Anthracite Co., Trevorton, Northumberland County, Pennsylvania
 Anthracite, Dorrance Mine, Lehigh Valley Coal Co., Luzerne County, Pennsylvania
 Cannel coal, Mine 27, Island Creek Coal Co., Logan County, West Virginia

Table 4. Evolution of gas from vitrains during the dehydrogenation process

Run No.	Vitrain	Stirring	Gross gas evolved, ml ^a				
			1 h	1.5 h	2 h	2.5 h	5.5 h
8R-61	Harmatten	Hershberg	62	84	100	111	155
8R-184	Harmatten	Magnetic	66	104	122	134	172
8R-109	Bruceton	Hershberg	51	77	92	104	147
8R-172	Bruceton	Magnetic	60	85	95	111	148
7R-167	Pocahontas No. 3	Hershberg	26	33	38	41	60
8R-182	Pocahontas No. 3	Magnetic	37	48	55	61	83

^a Approximate value for total gas evolved by the sample at the end of the indicated time, corrected to room conditions (ca. 25°C and 740 mm Hg pressure). The time given is from the beginning of the run; since the reaction mixture takes about one-half hour to reach operating temperature, the actual reaction time is about 0.5 h less than the time given. No correction for gas composition has been made.

Table 2. Analyses (moisture-free basis) of vitrains used for dehydrogenation

Run No.	Vitrain	C	H	N	S	Ash	O (by difference)	C, maf
9R-32	Beulah-Zap (Zap Mine)	64.18	5.28	0.85	0.58	5.35	23.76	67.81
8R-190	Kincade	64.96	4.59	.61	.55	4.73	24.56	68.19
9R-40	Beulah-Zap (Beulah Mine)	66.45	5.40	.31	1.40	3.60	22.84	68.93
9R-42	Roland-Smith (Wyodak)	62.76	5.35	1.01	1.14	10.58	19.16	70.19
9R-3	Dietz (Big Horn)	68.55	4.90	.99	.57	3.23	21.76	70.84
9R-134	Laramie (Washington)	68.11	5.30	1.57	.45	4.80	19.77	71.54
9R-132	Pioneer Canon No. 1	68.75	5.07	.90	1.25	5.23	18.80	72.54
8R-156	Rock Springs	73.21	5.17	1.38	.80	.66	18.78	73.70
8R-161	Illinois No. 6 (Green Diamond)	74.30	5.56	1.13	2.52	1.79	14.70	75.65
8R-162	Illinois No. 6 (Mecco)	74.71	5.39	1.03	2.05	1.77	15.05	76.06
9R-34	No. 11 (Rainbow No. 7)	75.54	5.63	1.92	.84	1.28	14.79	76.52
8R-184	Illinois No. 7 (Harmatten)	75.79	5.29	1.31	1.76	1.03	14.82	76.58
9R-41	Liberty	73.72	5.85	1.65	.72	5.06	13.00	77.65
8R-186	Illinois No. 6 (Orient No. 3)	77.64	5.16	1.87	1.14	1.89	12.30	79.14
8R-159	Kentucky No. 9 (Pleasant View)	78.12	5.89	1.58	1.97	1.54	10.90	79.34
8R-158	Kentucky No. 9 (DeKoven)	78.59	5.81	1.30	2.04	2.61	9.65	80.69
8R-143	Pittsburgh (Bruceton)	81.72	5.50	1.27	1.30	1.65	8.56	83.09
8R-172	Pittsburgh (Bruceton)	81.72	5.50	1.27	1.30	1.65	8.56	83.09
8R-147	Pittsburgh (Bruceton)	81.72	5.50	1.27	1.30	1.65	8.56	83.09
8R-149	Pittsburgh (Bruceton)	81.72	5.50	1.27	1.30	1.65	8.56	83.09
8R-160	Pond Creek (Majestic)	82.41	5.48	1.34	.81	1.59	8.37	83.74
8R-187	Powellton (Elk Creek No. 1)	84.46	5.28	1.53	.96	.69	7.08	85.05
8R-157	Eagle (Kopperston)	84.44	5.52	1.45	.97	2.03	5.59	86.19
8R-165	Sewell (Lochgelley)	85.74	5.20	1.44	.79	.79	6.04	86.42
8R-176	Lower Freeport (Coal Valley No. 7)	85.17	5.13	1.42	1.15	2.42	4.71	87.28
8R-175	Lower Kittanning (Melcroft)	85.34	5.00	1.51	1.46	2.32	4.37	87.37
8R-167	Lower Banner (Buccaneer)	85.37	5.23	1.29	.71	3.42	3.98	88.39

(Continued)

Run No.	Vitrain	C	H	N	S	Ash	O (by difference)	C, maf
8R-164	Sewell (Marianna)	88.15	5.00	1.43	.77	.88	3.77	88.93
8R-174	Beckley (Maben)	87.79	4.70	1.60	1.12	1.29	3.50	88.94
8R-166	Sewell (Crab (Orchard)	87.79	4.99	1.36	.59	1.68	3.59	89.29
9R-133	Lower Hartshorne	86.06	4.80	1.70	.73	3.87	2.84	89.52
8R-185	Upper Kittanning (Stineman No. 10)	87.64	4.84	1.44	.87	2.70	2.51	90.07
8R-181	Pocahontas No. 4 (McAlpine)	89.23	4.59	1.49	.81	1.15	2.73	90.27
8R-183	Lower Kittanning (Toth)	88.35	4.82	1.32	.74	2.34	2.43	90.47
8R-182	Pocahontas No. 3 (Buckeye No. 3)	89.57	4.67	1.25	.81	1.53	2.17	90.96
9R-119	Semianthracite (Bernice) ^a	79.22	3.43	1.01	.65	11.97	3.72	89.99
9R-118	Semianthracite (Western Middle) ^b	77.55	3.42	1.25	.85	14.36	2.57	90.55
8R-189	Dorrance anthracite	91.06	2.49	.96	.83	1.79	2.87	92.72
8R-188	Cannel coal ^c	79.93	6.44	1.69	1.05	4.55	6.34	83.74

^a Whole coal, ca. 25 per cent vitrain (see text).

^b Whole coal, over 90 per cent vitrain (see text).

^c Whole coal.

Table 3. Results of dehydrogenation with phenanthridine as vehicle and 1 per cent palladium on calcium carbonate catalyst^a

Run No.	Vitrain	C, maf	Per cent		H evolved, ml/g ^d	H/C atomic	O/C atomic
			H ₂ evolved ^b	H/100 C evolved ^c			
9R-32	Beulah-Zap (Zap Mine)	67.81	26.6	26.1	165	0.981	0.278
8R-190	Kincade	68.19	26.1	21.9	140	.842	.284
9R-40	Beulah-Zap (Beulah Mine)	68.93	39.2	38.0	244	.969	.258
9R-42	Roland-Smith (Wyodak)	70.19	26.7	27.2	178	1.016	.229
9R-3	Dietz (Big Horn)	70.84	33.9	28.9	191	.852	.238
9R-134	Laramie (Washington)	71.54	24.5	22.8	152	.928	.218
9R-132	Pioneer Canon No. 1	72.54	30.6	26.9	182	.879	.205
8R-156	Rock Springs	73.70	31.2	26.3	181	.842	.193
8R-161	Illinois No. 6 (Green Diamond)	75.65	39.0	34.8	246	.892	.149
8R-162	Illinois No. 6 (Mecco)	76.06	38.9	33.4	238	.860	.151
9R-34	No. 11 (Rainbow No. 7)	76.52	43.6	38.7	277	.888	.147
8R-184	Illinois No. 7 (Harmatten)	76.58	44.0	36.6	262	.832	.147
9R-41	Liberty	77.65	45.1	42.6	310	.946	.132
8R-186	Illinois No. 6 (Orient No. 3)	79.14	37.1	29.4	217	.792	.119
8R-159	Kentucky No. 9 (Pleasant View)	79.34	39.1	35.1	260	.899	.105
8R-158	Kentucky No. 9 (DeKoven)	80.69	35.4	31.2	235	.881	.0922
8R-143	Pittsburgh (Bruceton)	83.09	37.4	30.0	232	.802	.0786
8R-172	Pittsburgh (Bruceton)	83.09	37.1	29.8	231	.802	.0786
8R-147	Pittsburgh (Bruceton)	83.09	35.7	28.7	222	.802	.0786
8R-149	Pittsburgh (Bruceton)	83.09	37.0	29.7	230	.802	.0786
8R-160	Pond Creek (Majestic)	83.74	33.5	26.6	207	.793	.0762
8R-187	Powellton (Elk Creek No. 1)	85.05	35.3	26.3	209	.745	.0629
8R-157	Eagle (Kopperston)	86.19	29.0	22.6	182	.779	.0497
8R-165	Sewell (Lochgelley)	86.42	27.4	19.8	160	.723	.0529
8R-176	Lower Freeport (Coal Valley No. 7)	87.28	26.3	18.9	154	.718	.0415
8R-175	Lower Kittanning (Melcroft)	87.37	28.3	19.7	160	.698	.0384

Continued

Run No.	Vitrain	C, maf	Per cent H ₂ evolved ^b	H/100 C evolved ^c	H evolved, ml/g ^d	H/C atomic	O/C atomic
8R-167	Lower Banner (Buccaneer)	88.39	24.0	17.5	144	.730	.0350
8R-164	Sewell (Marianna)	88.93	22.3	15.1	126	.676	.0321
8R-174	Beckley (Maben)	88.94	21.6	13.8	115	.638	.0299
8R-166	Sewell (Crab Orchard)	89.29	19.6	13.3	110	.678	.0307
9R-133	Lower Hartshorne	89.52	20.5	13.6	114	.665	.0248
8R-185	Upper Kittanning (Stineman No. 10)	90.07	21.3	14.0	118	.658	.0215
8R-181	Pocahontas No. 4 (McAlpine)	90.27	19.1	11.6	99	.613	.0230
8R-183	Lower Kittanning (Toth)	90.47	21.2	13.8	116	.650	.0206
8R-182	Pocahontas No. 3 (Buckeye No. 3)	90.96	22.5	14.0	119	.621	.0182
9R-119	Semianthracite (Bernice)	89.99	1.0	.5	5	.516	.0353
9R-118	Semianthracite (Western Middle)	90.55	2.4	1.2	11	.526	.0249
8R-189	Dorrance anthracite	92.72	0.0	0.0	0	.326	.0237
8R-188	Cannel coal	83.74	30.2	29.0	227	.960	.0595

^a All runs used catalyst lot C-2842 except for 8R-147, 149 which used lot 7902.
All runs used magnetic stirring. Samples were -200 mesh.

^b Per cent of hydrogen in starting material which is evolved as H₂ gas.

^c Atoms of hydrogen evolved as H₂ gas per 100 C atoms in starting material.

^d Milliliters of hydrogen gas evolved per gram of m.a.f. starting material.

In Table 2, the four runs on Pittsburgh (Bruceton) vitrain gave some idea of the reproducibility which can be expected. The first two runs are with one batch of catalyst, the second pair is with another batch of catalyst. (All of the other runs listed were made with the same catalyst used for the first pair on Bruceton vitrain.)

Figure 1 shows the hydrogen evolution as a function of carbon content (maf) of the starting vitrain. In discussing this, it should be noted that the system used for classification of coals according to rank^{19,20} is not based upon the chemical structure of the coal. Instead, rank classification is based partly upon fixed carbon (which is not directly related to the carbon content determined by a standard combustion analysis), partly upon volatile matter (which again does not correspond to any usual chemical determination), partly upon Btu content (which of course is related, but in no specific way, to chemical composition), and partly upon agglomeration properties. In Figure 1, for 24 vitrains, all obtained from coals ranging in rank from high volatile C bituminous to low-volatile bituminous, the data scatter about a reasonably smooth curve, in which the hydrogen evolution decreases gradually as the carbon content increases from 75.7 percent maf to 91.0 percent maf. Three other points, for semianthracite and anthracite, suggest that the hydrogen evolution decreases rapidly for ranks above low-volatile bituminous, reaching zero for an anthracite. This is reasonable; it is generally agreed that the coalification process involves an increase in the aromatic nature of the coal, and it is not surprising that, by the time anthracite is reached, there are no hydroaromatic structures remaining in the coal.*

The low rank vitrains do not seem to fall on the same curve defined by the vitrains from bituminous coals. Two of the three lignite vitrains and all five of the subbituminous vitrains fall well below the band established by the bituminous vitrains. This difference can be brought out more clearly by plotting the hydrogen evolved (H/100 C) against the atomic H/C ratio, or even better, against the atomic O/C ratio, of the vitrain. These two graphs are shown in Figures 2 and 3. In Figure 2, it can be seen that a plot of H/100 C against H/C ratio gives a fairly good straight line for the 24 bituminous vitrains. The solid line shown is a least squares straight line for these 24 points. The equation of the line is given by: $H/100 C = 93.11 (H/C) - 46.68$. For the straight line, the standard error of estimate is 2.54; the multiple correlation coefficient is 0.966. The dashed lines on either side of the solid line are at distances of twice the standard error of estimate; this means that 95 percent of the points should lie within the two dashed lines. Put in other words, if a point lies outside the area between the two lines formed by the twice standard error, there is only a probability of 1/20 that this point belongs with the set of data used to draw the least squares line. It can be seen that one subbituminous falls within the area; one lignite and one subbituminous fall barely outside; and the other three subbituminous and two lignites fall outside of the area.

*Cannel coal is included on the graph for the sake of completeness; it is an atypical whole coal and will not be discussed.

Figure 3 is a similar plot of H/100 C against the O/C ratio. For the 24 bituminous vitrains, the equation of the least squares straight line is: $H/100 C = 190.5 (O/C) + 10.51$. For this straight line, the standard error of estimate is 3.20; the multiple correlation coefficient is 0.946. Since the oxygen analysis is by difference, it is subject to a larger error than are the other analyses. The O/C ratio is therefore less accurate than the H/C ratio, and the increased standard error and decreased multiple correlation coefficient for the O/C curve (as compared with the H/C curve) is to be expected.

In Figure 3, it is seen that all of the lignite and subbituminous points fall well outside the area of twice the standard error. For any one lignite point, the probability of it belonging with the bituminous straight line is 1/20; therefore, it might be said that the probability of all three lignite vitrains belonging to the bituminous set is 1/8000, or 0.000125. There is an even lower probability that all five subbituminous vitrains belong with the bituminous set. It is significant that all eight points fall on the same side of the least squares straight line.

Another approach to the data has been to find the least squares straight line for the combined 32 points (24 bituminous, 5 subbituminous, and 3 lignites). The equation for this line (which is not shown in any figure) is: $H/100 C = 59.1 (O/C) + 18.1$. For this line, the standard error of estimate has increased to 7.25; the multiple correlation coefficient has decreased to 0.581. The standard error has thus more than doubled, and the multiple correlation coefficient has decreased greatly. This again indicates that the subbituminous and lignite vitrains are not part of the bituminous group.

From the above discussion we may draw the following conclusion: that there is a fundamental chemical difference between bituminous coals on the one hand, and subbituminous coals and lignites on the other hand. This difference manifests itself in the amount of hydrogen gas produced by catalytic dehydrogenation in the presence of a solvent. This, in turn, must be related to the general structure of the coal and in particular to its hydroaromaticity. Thus, although a high volatile C bituminous coal and a subbituminous A coal are distinguished from each other solely on the basis of calorific limits and agglomerating properties^{19,20}, there must nevertheless be a real difference in their chemical structure.

One may wonder why this demarcation is more obvious in the O/C plot (Figure 3) than it is in the H/C plot (Figure 2). One possible explanation is that for the entire bituminous group of coals, the hydrogen varies only slightly, being in the range of 4.5 to 6.0 percent; the carbon, however, varies from 68 to 90 percent. On the other hand, the oxygen and carbon values both vary considerably, and they vary in opposite directions; so that the O/C plot is probably a more sensitive indication of the structural change.

We come now to a consideration of the reasons for the sharp difference between the bituminous coals and lower rank coals, as shown by dehydrogenation. It is generally assumed that one of the major reactions of the coalification process is aromatization²¹. A decreasing yield of hydrogen obtained from coals of increasing rank can be simply explained on the basis of the higher rank coals being more aromatic. The low yield of hydrogen from low rank coals remains to be explained, however. At first thought, one is inclined to assume that a process of continual aromatization must by its very nature also be a process of dehydroaromatization; that is, aromatization should cause loss of

hydroaromatic structures. This is not true, however, because aromatization may take place by changes in structures which are not themselves hydroaromatic. A schematic representation (Figure 4) illustrates a possible series of reactions for this process. The \textcircled{R} portion is intended to represent the bulk of a coal molecule, with attention focused on the ring system attached to it. In structure (I), there is no hydroaromatic system (as per the definition given above) and no normal dehydrogenation can take place; the angular methyl group slows aromatization³, since it must either migrate or be eliminated before dehydrogenation can take place. If the natural coalification process involves an aromatization* we may presume that the methyl group either migrates from the angular 9-position, which permits easy dehydrogenation to (II) and then further dehydrogenation to (IV); or alternatively the methyl group is eliminated from (I) as methane, which permits dehydrogenation to (III) and then further dehydrogenation to (V). We may consider (I) as corresponding to lignites and sub-bituminous coals; high hydrogen but no hydroaromatic structures. We may consider (II) and (III) as corresponding to bituminous coals; in the process of coalification (I \rightarrow II + III) there has been simultaneous formation of aromatic structures and of dehydrogenatable hydroaromatic structures. Thus we have a model for a process in which a non-hydroaromatic structure (I) is partly aromatized to give aromatic structures which also contain hydroaromatic rings. In a continuation of the coalification process, (II) and (III) are aromatized to (IV) and (V), which are completely aromatic (anthracite) and hence cannot give any hydrogen gas upon treatment with a dehydrogenation catalyst. This greatly simplified series of reactions, I \rightarrow II \rightarrow IV and I \rightarrow III \rightarrow V, offers a model for the seemingly peculiar situation in coal, where very low rank coals yield less hydrogen than do some higher rank, more aromatic coals.

It must be emphasized that the mechanism in Figure 4 is very schematic, is capable of many variations, and that several of these variations might proceed simultaneously. For example, the blocking group in the 9-substituted decalin structure (I) need not be methyl; it could be other groups, e.g., carboxyl. The blocked low rank structure (I) could be a 1,1-disubstituted cyclohexane type, which would undergo a similar series of transformations, or it could be a bridged six membered ring of the bicycloheptane type.

While this theory is not without its attractiveness, it may be asked whether coal can reasonably be expected to contain blocked structures of the type of (I). Coal is usually considered to arise by changes in the lignin and perhaps in the cellulose of the plant material which is its precursor²¹. Neither lignin nor cellulose contains polycyclic structures of the type of (I). Lignin contains benzene rings with reactive side chains. It is quite possible to visualize formation of condensed ring systems from cellulose, from lignin, or from an interaction of the two. Further, many plants contain appreciable amounts of other materials† more closely related in structure to (I). These include tricyclic diterpenes (abietic acid types), pentacyclic triterpenes (amyrin types), and tetracyclic sterols (stigmaterol and lanosterol types), which contain 1,1-dimethyl groups and angular methyl groups; and bicyclic terpenes

*For the purpose of this discussion we neglect the detailed mechanism of the coalification process and do not consider the loss of oxygen (perhaps as water) which takes place during coalification.

† The structures of some of these compounds are shown in Figure 5.

(pinene and camphane types) which contain bridged rings and 1,1-dimethyl groups. Also to be considered are some of the complex polycyclic alkaloids containing heterocyclic nitrogen, which occur in large amounts in some plants. It is possible that compounds of these types play a more important part in the coalification process than has heretofore been realized.

It remains to consider three possible sources of error in the hydrogen values obtained, all of which we believe are minor. These are interaction of the coal with the vehicle; cross-linking of coal structures during dehydrogenation, with formation of hydrogen*; and effect of phenolic groupings in the coal. It is known that the vehicle reacts with the coal, and it has so far proven impossible to remove all of the phenanthridine from a dehydrogenated coal¹². Obviously, the reaction: $\text{Coal-H} + \text{Vehicle-H} \rightarrow \text{Coal} \sim \text{Vehicle} + \text{H}_2$ would lead to a high value for hydrogen liberated. However, vehicle-vitrain blanks have been shown to be negligible and vehicle-catalyst blanks have been deducted, although this does not preclude interaction between coal and vehicle in the presence of catalyst. In addition, a reaction of the type: $\text{Coal-H} + \text{Vehicle-H} \rightarrow \text{H-Coal} \sim \text{Vehicle-H}$ would also account for the impossibility of removing vehicle from dehydrogenated coal and yet would not lead to hydrogen formation. Further experiments may throw some light on this process. We do know that one vehicle (1-azapyrene) liberates large amounts of hydrogen when heated only with a catalyst and that at least one other vehicle (2-azafluoranthene) gives very high values for hydrogen evolution from coal¹¹ which are almost certainly incorrect. Nevertheless, there is no real reason to believe that the phenanthridine contributes significantly to the evolved hydrogen, although this possibility must be kept in mind. Second, there is the question of "cross-linking," a somewhat vague term implying chemical reaction between two coal platelets. Here again, there are two possible reactions analogous to the two given above:



The first of these would lead to extra evolution of hydrogen, the second would not. The insolubilization of the coal which takes place during dehydrogenation could be used as an argument in favor of cross-linking; however, one might reasonably expect the dehydrogenated coal to be less soluble than the starting material in any case. Third, we have found that certain phenolic compounds yield hydrogen, probably by reactions of the type



This reaction can be eliminated by the use of the silyl ethers in place of the free phenols. However, there is some evidence (based on the dehydrogenation of silyl ethers of phenols) that the phenolic groups in coal give little or no hydrogen, and that this side reaction is of slight consequence in coal dehydrogenation.

*Infrared spectra did not yield any useful information. The presence of vehicle; the small number of protons; and the difficulty of grinding; all contribute to loss of spectral information. A similar situation was found by Friedel and Breger²² for a cross-polymerized coal formed by neutron irradiation.

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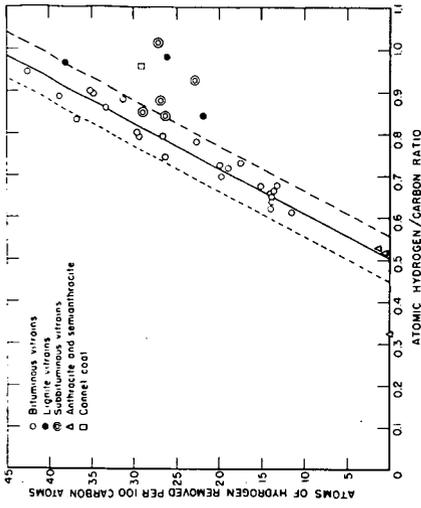


Figure 2.-Dehydrogenation of vitrains with one percent palladium on calcium carbonate catalyst, phenanthridine vehicle, plotted as a function of the atomic H/C ratio. The solid line is the least squares straight line for the 24 bituminous vitrains. The dashed lines are drawn at a distance of twice the standard error of estimate.

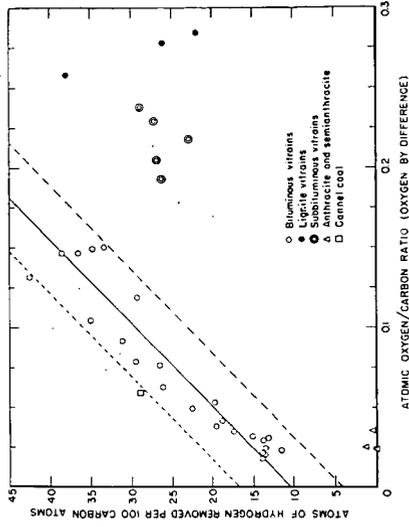


Figure 3.-Dehydrogenation of vitrains with one percent palladium on calcium carbonate catalyst, phenanthridine vehicle, plotted as a function of the atomic O/C ratio (oxygen analysis by difference). The solid line is the least squares straight line for the 24 bituminous vitrains. The dashed lines are drawn at a distance of twice the standard error of estimate.

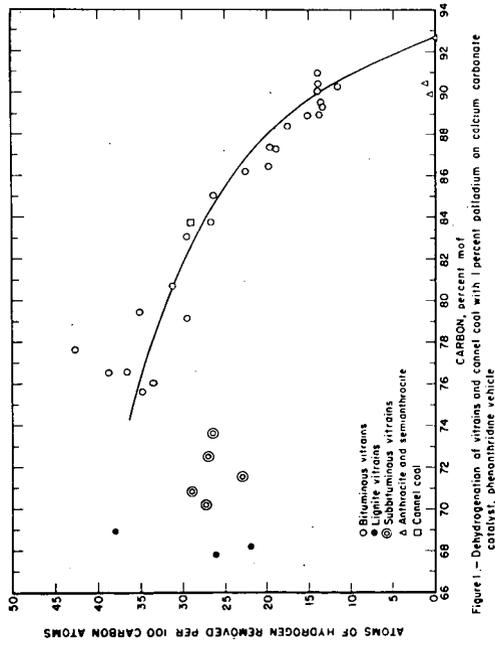


Figure 1.-Dehydrogenation of vitrains and cannel coal with 1 percent palladium on calcium carbonate catalyst, phenanthridine vehicle

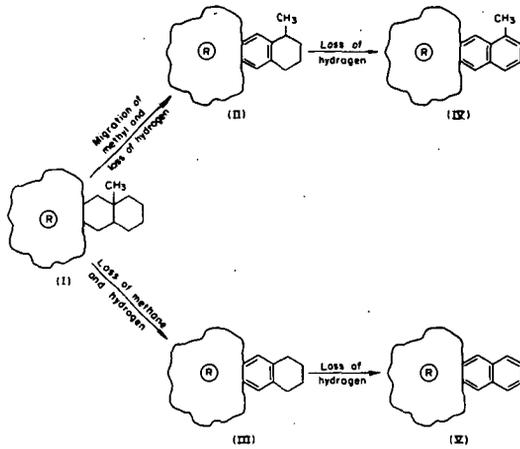


Figure 4.-Schematic representation of the coalification process.

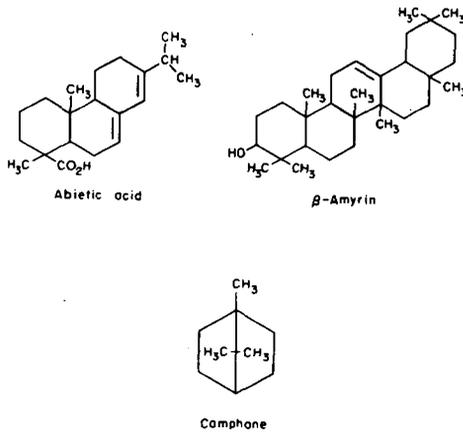


Figure 5-Structures of compounds found in plants which may be coal precursors (see text)