

age deviations of the s/s_0 averages to be certainly not much better than 0.5% for our measurements nor than 1.0% for Karle and Brockway's. (It would be entirely misleading to include the very widely deviating measurements of the third minimum and third maximum in this consideration of the respective s_0 scales because it is obvious that these deviations are simply representations of the extremely different qualitative interpretations made of these features in the two investigations.) To express this matter in still another way, Karle and Brockway's measurements for the second maximum and the consecutive features from the fourth maximum to the seventh minimum lead with our model BB to an average $q_{\text{calc.}}/q_0$ of 1.002, in excellent agreement with our averages.

NOTE ADDED OCTOBER 20, 1947.—On the basis mainly of spectroscopic data Van Zandt Williams has recently reported¹¹ the following complete set of structural parameters for the formic acid monomer molecule, which, he concludes, is planar

C—H = 1.08 ± 0.01 Å., O—H = 0.96 ± 0.01 Å., C=O = 1.225 ± 0.02 Å., C—O = 1.41 ± 0.02 Å., ∠O—C=O = 125 ± 1°, ∠C—O—H = 107 ± 5°, and ∠H—C=O = 122 ± 5°.

The rather poor agreement between the electron diffraction results and Williams' values can be reexpressed significantly in terms of the principal moments of inertia, which are more directly related to the spectroscopic data. Our value for the small moment of inertia (assuming Williams' hydrogen-atom parameters) is very nearly equal to Williams' but is considerably different from Karle and Brockway's; however, the electron diffraction values for the intermediate moment of inertia, which depends essentially on the O...O distance, are in agreement and

(11) Van Zandt Williams, *J. Chem. Phys.*, **15**, 232 (1947).

about 5% smaller than Williams'. The parameters of Williams' model which define the small moment of inertia are well confirmed by measurements on several absorption bands of HCOOH^{11,12,13} and its three deuterated derivatives¹¹; on the other hand, Williams' value for the intermediate moment is derived from Bauer and Badger's determination¹² of the rotational fine-spacing constant δ , which, depending on the interpretation of one incompletely band, may possibly¹⁴ be in error by more than the original estimate of 1%, and the disagreement with our model involves just the parameter —O...O— for which (we have argued above) there is significant agreement between the two electron diffraction investigations.

Acknowledgment.—We are indebted to the International Business Machines Corporation for the loan of the equipment used in making the radial distribution function and intensity function summations.

Summary

The structure of formic acid monomer has been reinvestigated by electron diffraction, using a new type of heated nozzle to introduce the sample into the camera. The parameter values found are C=O = 1.213 ± 0.026 Å., C—O = 1.368 ± 0.034 Å., O...O = 2.275 ± 0.025 Å., ∠O—C=O = 123½ ± 3°, and C—O/C=O = 1.127 ± 0.018. The arguments leading to these values are given in relatively great detail, and a careful effort is made to explain the probable nature of the errors that led to considerably different results in an earlier investigation.²

(12) S. H. Bauer and R. M. Badger, *J. Chem. Phys.*, **5**, 853 (1937).

(13) H. W. Thompson, *ibid.*, **7**, 453 (1939).

(14) Private communication from Professor Badger.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Reaction of Coal with Oxygen in the Presence of Aqueous Sodium Hydroxide. Effect of Methylation with Dimethyl Sulfate¹

BY G. R. YOHE² AND EVA O. BLODGETT³

If pulverized bituminous coal is suspended in aqueous alkali and subjected to the action of oxygen at elevated temperatures and pressures, the coal substance can be converted practically completely to carbon dioxide and a mixture of relatively simple acids in which aromatic polycarboxylic acids predominate. Smith, Tomarelli and Howard subjected various coals to this type of oxidation at 100–250° with oxygen under pressures of 100–300 pounds per square inch⁴; Franke and Kiebler operated at 200–300° with total pressures of 500–1200 pounds per square inch

and obtained an acid product of average equivalent weight of 80 and an average molecular weight of 250.⁵ The use of much milder conditions, however, results in a much slower reaction and less far-reaching degradation of the coal substance. Smith, Tomarelli and Howard noted a very slow reaction rate below 225°⁴; other work has shown that when air is bubbled through a suspension of coal in aqueous sodium hydroxide at 95 ± 5° for three weeks, the principal product in the case of bright coals is humic acid.⁶ The literature on oxidation of coal has recently been summarized by Howard.⁷

(1) Presented before the Division of Gas and Fuel Chemistry, Atlantic City, N. J., April 17, 1947. Published with permission of the Chief, Illinois State Geological Survey.

(2) Chemist, Illinois State Geological Survey.

(3) Formerly Research Assistant. Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

(4) R. C. Smith, R. C. Tomarelli and H. C. Howard, *THIS JOURNAL*, **61**, 2398–2402 (1939).

(5) N. W. Franke and M. W. Kiebler, *Chem. Ind.*, **58**, 580–581 (1946).

(6) G. R. Yohe and C. A. Harman, *Trans. Illinois Acad. Sci.*, **82**, 134–136 (1939).

(7) H. H. Lowry, editor, "Chemistry of Coal Utilization," Vol. I, John Wiley and Sons, New York, N. Y., Chap. 9, pp. 346–376.

Little is known as to the nature of the chemical structures or functional groups which are first attacked in these oxidation reactions. Tronov has propounded a theory that atmospheric oxygen attacks phenolic structures in the coal substance.⁸ If this is true, then the protecting of phenolic groups by conversion to the methyl ethers should decrease the susceptibility of coals to attack by oxygen. This paper presents the results of a series of experiments in which coals of various ranks and also their products obtained by methylation with dimethyl sulfate have been oxidized. Under the conditions used, various phenols were attacked by oxygen, but the methyl ethers tested have been resistant.

Experimental

Apparatus

The Reaction Vessel.—The reaction vessel was a stainless steel cylinder of approximately 470 ml. capacity (5.7 cm. inside diameter, 18.4 cm. high) surrounded by a brass jacket. The jacket space was attached to a reflux condenser by means of a flexible coupling, and water therein was kept at the boiling temperature by means of a wound-on electric heater, thus maintaining constant temperature in the inner reaction vessel. The oxygen inlet tube was attached by means of a flanged coupling and rubber gasket secured by a screw collar. The vessel was mounted upright in a cradle and agitated by a mechanism similar to that commonly used for catalytic hydrogenations.⁹

The Oxygen Reservoir.—A 20-liter carboy bottle was used for an oxygen reservoir. It was fitted with a mercury manometer and a long-stem thermometer with the bulb at the center of the bottle; a tube leading to the bottom of the bottle made it possible to fill the reservoir with oxygen by displacement of water. The rubber stopper that carried the thermometer and delivery tubes was sealed with gasket shellac and wired in.

Connector.—Figure 1 shows the valve and stopcock arrangement that was used to connect the oxygen reservoir at A to the reaction vessel at H. Offsets at B and D place the valve mechanism CE about 3 cm. behind the plane of A-F-H.

The entire apparatus was constructed in duplicate and both reaction vessels were agitated by the same motor and mechanism.

Pressure and temperature readings were taken each morning before doors or windows were opened; it was not found necessary to place the oxygen reservoirs in a constant temperature bath.

Procedures

The Oxidation Experiments.—The water jacket was half-filled with distilled water and the reflux condenser attached. The weighed coal sample (3.000 to 5.000 g.) was placed in the reaction vessel, 250 ml. of 5% sodium hydroxide added, the vessel was closed and flushed with oxygen by alternately evacuating through the horizontal arm of the 3-way cock G and filling with oxygen from the reservoir by manipulation of 3-way cock F while the ground glass valve C was kept closed by raising a mercury leveling bulb attached at E. When this was completed, the vacuum connection to the horizontal arm of G was replaced by a tube from the oxygen cylinder and the oxygen pressure in the system was raised to about 150 mm. above atmospheric. Then stopcock F was mercury-sealed by raising a leveling bulb attached at the vertical arm of G, and valve C was opened by lowering the bulb attached

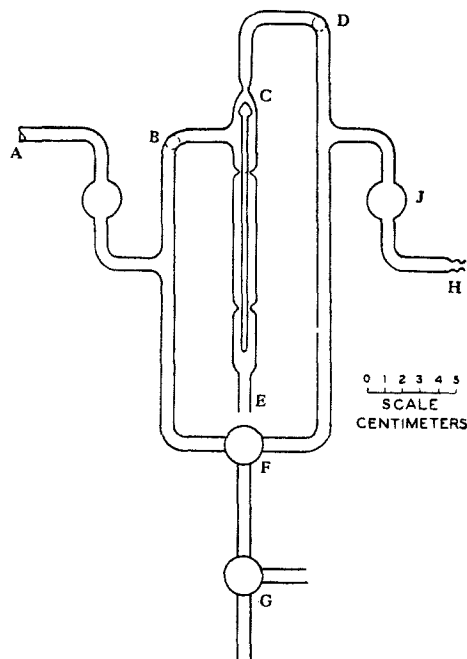


Fig. 1.—System used to connect oxygen reservoir with reaction vessel

at E. It was found necessary to mercury-seal all stopcocks to prevent slow leakage over the extended times that these oxidations were run.

A "cold" reading of pressure, temperature, and barometric pressure was taken and the volume of oxygen in the reservoir was corrected to standard conditions, including correction for the presence of water vapor. When repeat readings after quarter to half hour checked, the heater was turned on and the shaker started. With some coals there was a tendency for the reaction mixture to foam back into the oxygen inlet tube at the start, so the temperature was ordinarily raised slowly so that from half to one hour was required to bring the water in the jacket to boiling. Readings were usually taken every few hours at the start of a run and daily thereafter for a period of about three weeks.

As the pressure in the system was increased by heating the reaction vessel, there was an apparent increase in the oxygen content if oxidation proceeded slowly. At the end of the run the heater and shaker were turned off, allowed to come to room temperature, and a final "cold" reading was taken. The values for oxygen remaining in the reservoir, and hence the amounts of oxygen used by the sample at all readings during the run were later corrected for this apparent increase. The vapor pressure of water above a 5% sodium hydroxide solution at 100° is 30 millimeters lower than that of pure water.¹⁰

Methylation of Coals.—All coals were methylated by the procedure described here for vitrain. Although quantities treated were different for different preparations, the proportions used were the same.

To twenty-five grams of minus 200-mesh vitrain mixed with a solution of 12.8 g. of sodium hydroxide in 65 ml. of water and heated nearly to boiling, 20 g. of dimethyl sulfate was added in small portions with stirring. The mixture was refluxed for two hours and then treated again with like quantities of sodium hydroxide solution and dimethyl sulfate. After a second two-hour reflux period, the methylated coal was washed with water by centrifuging and decanting several times, collected on a filter, washed repeatedly, and dried. The yield of methylated vitrain was 24.4 g.

(8) B. V. Tronov, *J. Applied Chem. (U. S. S. R.)*, **13**, 1053-1058, 1059 (1940); *C. A.*, **35**, 1966 (1941).

(9) Roger Adams and V. Voorhees, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, New York, N. Y., 1941, pp. 61-67.

(10) "Handbook of Chemistry and Physics," 20th ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1945, p. 1814.

TABLE I
 ANALYTICAL DATA, COALS

Coal	Seam	County and state	As received		Ultimate composition, %						Calorific value, cal./g. ^a
			Moisture, %	Ash, %	Moisture- and ash-free basis						
					C	H	N	O	S	Methoxyl	
Lignite	Coteau	Ward, N. D.	32.5	5.0	72.38	5.30	1.12	20.53	0.67	2.22	4477
Subbituminous B	Unnamed	Weld, Colo.	20.7	3.9	77.69	5.24	1.60	14.98	0.49	0.25	5818
High-volatile C bituminous	5	Fulton, Ill.	13.7	10.3	81.41	5.64	1.56	7.89	3.50	Trace	7005
High-volatile B (Vitrain) bituminous	6	Franklin, Illinois	5.4	2.2	81.96	4.98	1.65	10.23	1.18	Nil	7611
High-volatile A bituminous	Pittsburgh	Allegheny, Pa.	1.7	7.8	82.92	5.91	1.80	6.4	3.05	...	8352
Medium-volatile bituminous	Sewell	Fayette, W. Va.	1.4	1.8	89.47	4.93	1.66	3.49	0.45	...	8559
Low-volatile bituminous	Pocahontas 3	McDowell, W. Va.	0.6	7.4	91.36	4.60	1.24	2.07	0.73	...	8697
Anthracite	Lykens	Luzerne, Pa.	4.2	2.4	94.88	1.83	0.67	1.78	0.84	...	7878

^a Moist, mineral matter free. Multiply by 1.8 to get B. t. u. per pound values used in A. S. T. M. classification by rank.

 TABLE II
 ANALYTICAL DATA, METHYLATED COALS

Obtained from	As received		Ultimate analysis, %					
	Moisture %	Ash %	Moisture- and ash-free basis					
			C	H	N	O	S	Methoxyl
Lignite	14.2	8.6	72.37	5.45	1.10	20.61	0.47	8.33
Subbituminous B	24.6	4.8	77.24	5.30	1.67	15.45	.34	4.97
High-volatile C bituminous	7.9	7.5	80.22	5.80	1.57	8.92	3.49	3.96
High-volatile B bituminous (Vitrain)	2.4	2.1	81.15	5.51	1.52	10.72	1.10	8.19
High-volatile A bituminous	1.8	9.6	81.38	5.73	2.09	7.77	3.03	3.08
Medium-volatile bituminous	1.3	2.0	88.52	5.02	1.78	4.17	0.51	Trace
Low-volatile bituminous	1.0	7.0	91.08	4.68	1.33	2.19	.72	Trace
Anthracite	1.6	3.7	95.29	1.83	0.64	0.75	1.49	0.22

Analytical data for coals and methylated coals are given in Tables I and II.

It is recognized that this methylation of a solid insoluble material cannot be expected to convert the coal completely to its methylated derivative, as only the groups at or very near the surface of the particles can come in contact with the reagent. However, the writers believe that the results presented in this paper indicate that the methylation thus carried out introduced a sufficient number of methoxyl groups to be of significance in this study.

Discussion

The results of the oxidation experiments are shown graphically in the accompanying figures.

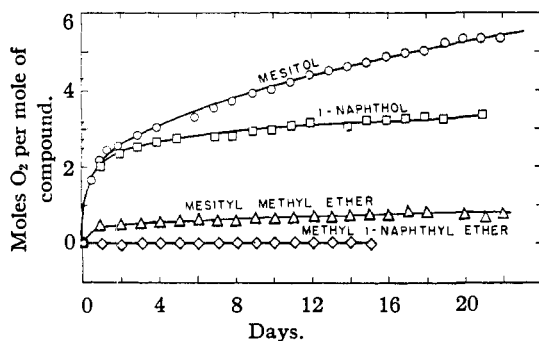


Fig. 2.—Effect of methylation on oxidation of mesitol and 1-naphthol.

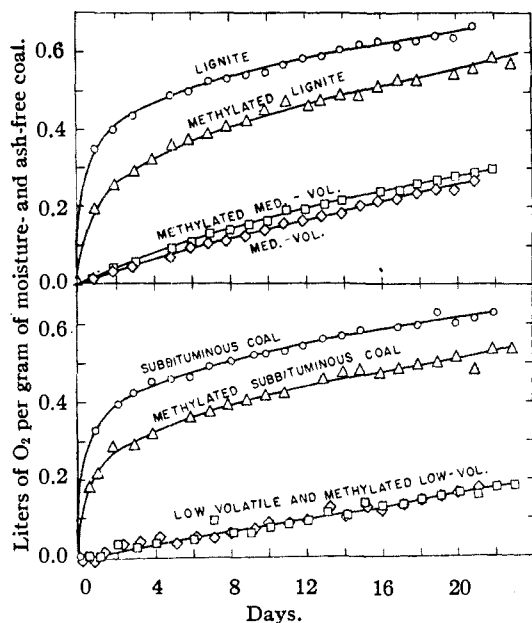
The effect of methylating phenolic compounds upon susceptibility to oxidation is shown in Fig. 2. Under the experimental conditions employed mesitol and naphthol oxidized rapidly; their methyl ethers were resistant. It seems possible that the mesityl methyl ether may have been con-

taminated with a small amount of oxidizable impurity such as mesitol itself.

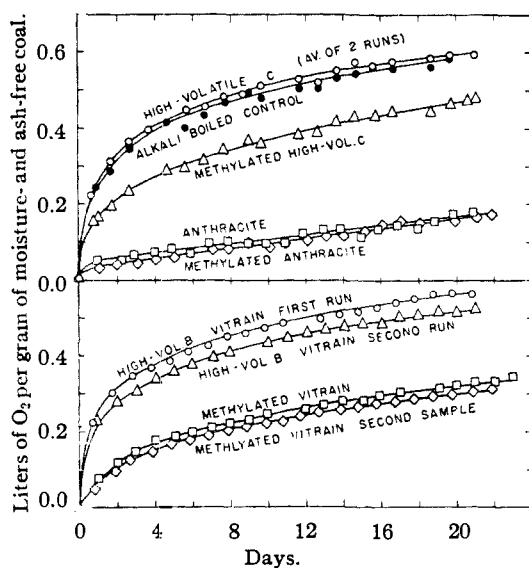
Inasmuch as the methylation procedure used involves boiling the suspension of coal in approximately 16% sodium hydroxide solution, the question was raised as to whether any effect noted might be due to the action of this alkali, rather than to the introduction of methoxyl groups. Experiments in which high-volatile C bituminous coal was compared not only with its methylated derivative, but also with a parallel sample which had been subjected to alkali boiling like that used in the methylation procedure but without the addition of the dimethyl sulfate show that it is the introduction of the methoxyl groups and not the treatment with the more concentrated alkali that causes the diminution in oxygen absorption (Fig. 3c). Similar comparative experiments with high-volatile B bituminous coal and with vitrain selected from it were made but they are not reported here because the methylated samples prepared were small, and the ash and moisture data were not obtained.

In its oxidation behavior, whole coal of high-volatile B bituminous rank was similar to the vitrain isolated therefrom.

Figures 3a to 3e show the curves of oxygen absorbed for time in days by coals of various ranks and by their methylated derivatives. The curve for high-volatile C coal shows the average values for two duplicate runs; plotted separately, the curves for these two runs were nowhere more than 0.03 liter of oxygen per gram of coal apart. The two runs on high-volatile B vitrain utilized



Figs. 3a (upper) and 3b.—Effect of methylation on oxidation of coals.



Figs. 3c (upper) and 3d.—Effect of methylation on oxidation of coals.

the same coal sample, but the lower curve was made two months after the upper one. The two curves for methylated vitrain represent two different methylations (see Table II), not duplicate oxidations of the same methylated sample. In the calculations for the differences between original and methylated coals, the means of the two vitrain and of the two methylated vitrain curves were used.

It will be noted that in general the coals of lower rank absorbed more oxygen than those of higher rank, but that the protection afforded by

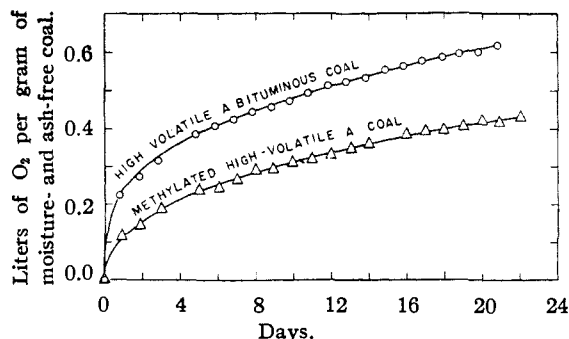


Fig. 3e.—Effect of methylation on oxidation of coal.

methylation measured in liters of oxygen per gram of coal is greater in the high volatile bituminous ranks than it is in the higher or lower classifications. In the medium volatile bituminous rank the methylated coal absorbed slightly more oxygen than did the original coal, but the difference is hardly great enough to be of significance. It will be noted from Table II that the amount of methoxy introduced into the medium and low volatile bituminous coals and the anthracite was very low.

If it be assumed that the decrease in oxygen absorption noted is due to the protection by methylation of certain structures, such as phenolic groups, then curves showing the differences in oxygen absorption between the original coals and their methylated derivatives should reveal the oxidation behavior of the groups that were protected. Figure 4 shows these difference values calculated to the basis of moles of oxygen consumed per equivalent of hydroxyl methylated. These curves show an

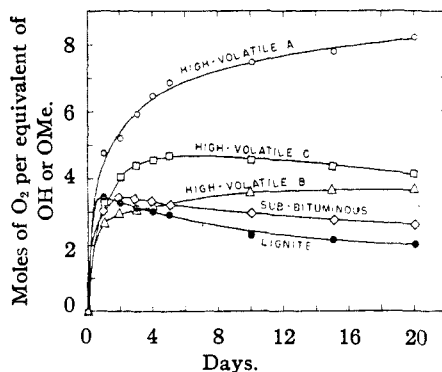


Fig. 4.—Difference in oxygen absorbed by coals and by methylated coals.

interesting progression in the amount of protection afforded per methoxyl group with change in rank. It will be noted that the high-volatile B and C bituminous coals are reversed in position, and that Fig. 5, which shows these same differences at ten days' oxidation time related to the oxygen content of the original coals, is free from this anomalous placing. The analysis of the high-volatile C coal shows a lower oxygen value than

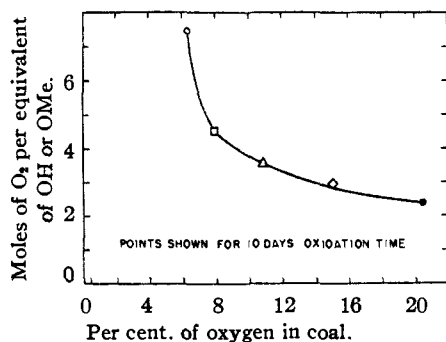


Fig. 5.—Difference in oxygen absorbed by coals and by methylated coals at ten days oxidation time.

would be expected, but a careful check of the analysis confirmed the value, a calculation of the calorific value from the ultimate analysis by the DuLong formula gave 7098 calories per gram as compared with 7005¹¹ shown in Table I, and a search of the laboratory files revealed other samples from the same region with comparable low oxygen values.

The fact that of the coals capable of being methylated, those of higher rank receive greater protection per methoxyl group suggests that with increasing rank, the phenolic structures involved may possess larger nuclei, *i. e.*, structures that require more oxygen to oxidize them, once oxidation has been initiated by way of the susceptible phenolic group.¹²

The downward trend shown by curves of the lower rank coals in Fig. 4 is of interest. This effect could conceivably result from competing oxidation reactions involving the same structural units through different susceptible functional groups. For example, if the relatively rapid reaction which in the original coal would attack by way of a phenolic group, is blocked by methylation, the destruction of the structural unit might still progress by means of a slower reaction introduced by way of some other functional group not capable of being protected by methylation, and the ultimate oxygen consumption of the methylated sample might approach that of the original coal.

Inasmuch as the procedure used in this study for methylating the coals is essentially the well-known method of converting phenols to their

(11) It is recognized that the difference between these calculated and determined values is somewhat higher than the average of such calculations, but it is small enough to confirm the essential correctness of the analytical data and the unexpectedly low value for the oxygen content of the coal.

(12) A study of the behavior of various phenols under similar conditions is being carried out in this laboratory. Although data are not yet sufficiently complete to publish, it has been shown that the oxidizability of phenols varies greatly with the number, position, and nature of substituent groups.

methyl ethers, a reasonable explanation of the results obtained would be that the low and medium rank coals contain phenolic structures which are susceptible to oxidation, whereas the higher rank coals (medium- and low-volatile bituminous and anthracite) contain very few or none of such structures. Although it is not likely that complete methylation of all phenolic groups was accomplished, it seems evident that these coals contain functional groups other than phenolic structures which are susceptible to oxidation under these conditions, for the methylated samples were still capable of absorbing appreciable quantities of oxygen. It is quite probable that the phenolic structures differ for the different ranks of coal and that in the low rank coals (lignite, subbituminous, and high-volatile C bituminous) structural units bearing phenolic hydroxyl groups are susceptible to oxidation by a competing mechanism, which is slower than that initiated by way of the phenolic hydroxyl.

Acknowledgments.—The writers are indebted to the Analytical Division of the Geo-chemical Section for the coal analyses and methoxyl determinations reported herein, and to Mr. A. W. Gotstein, machinist who constructed the reaction vessels and shaking mechanism. Thanks are also due to the following organizations which kindly provided the coal samples used: The Truax-Traer Coal Co.; the U. S. Bureau of Mines at Golden, Colorado; the United Electric Coal Corporation; the Chicago, Wilmington and Franklin Coal Co.; the Pittsburgh Coal Co.; the New River Coal Co.; the Koppers Co.; and the Stevens Coal Co.

Summary

Eight coals, ranging in rank from lignite to anthracite, have been subjected to oxidation by oxygen in the presence of 5% sodium hydroxide at 100°. Derivatives of these coals obtained by dimethyl sulfate methylation have been oxidized similarly.

The coals of high-volatile A bituminous rank and lower were capable of being methylated appreciably. Methylation reduced but did not completely remove the susceptibility to oxidation. It caused the greatest diminution in oxygen absorption per gram of coal in the high-volatile bituminous ranks; protection afforded per methoxyl group introduced varied inversely with the oxygen contents of the coals.

Medium- and low-volatile bituminous coals and anthracite did not methylate appreciably and treatment with the methylating reagent produced no significant change in oxygen absorption.