[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, THE PENNSYLVANIA STATE COLLEGE]

The Source of Acetic Acid Obtained by Oxidation of Coal

BY CORLISS R. KINNEY

It has been shown recently that bituminous coals, particularly the high volatile coals, have similar methane numbers.[1] This indicates that the common coals contain, in predominant amounts, similar structures regardless of variations in the kind or composition of the coal. These structures are also present in the lower rank coals, but appear to be less concentrated, probably because the deoxygenation has not proceeded so far. In the higher rank coals, the methane-yielding structures tend to decrease and have been largely destroyed in the case of true anthracites.

Acetic acid has been identified among the oxidation products of coal by many investigators and since both methane and acetic acid contain the methyl group it seems possible that the acetic acid is produced by the oxidation of groups which on carbonization yield methane. If this is correct, there should be a correlation between the yields of methane and acetic acid from various coals. Consequently, a quantitative method has been developed for determining the amount of acetic acid which may be obtained from coals and the results have been compared with the yields of methane obtained on carbonization. The method has also been applied to coals of varying rank, to certain petrographic constituents of coals, to plant materials, and to pure compounds in the hope that it would be possible to determine the kind of structures in coals and their petrographic constituents which yield acetic acid on oxidation.

Oxidation Procedure

Many methods of oxidizing coals and the substances from which they were formed have been used[2] but reagents which oxidize acetic acid or cause a rearrangement of the carbon structure before oxidation occurs should be avoided. For example cellulose has been oxidized in 27.7% yield by an alkaline pressure method,[3] but would be unsuited to the present purpose because it is obvious that the cellulose has undergone rearrangement reactions during the oxidation because cellulose does not contain the methyl group which is one of the characteristic groups in the structure of acetic acid. On the other hand, MacGregor, Evans and Hibbert[4] obtained only 0.05% acetic acid from cellulose using chromic acid oxidation, although acetic acid has been shown to resist oxidation by chromic acid.[5] Usually, aqueous solutions attack coals very slowly and for that reason it was decided to use concentrated nitric acid in conjunction with sodium or potassium dichromate. This mixture rapidly attacks all types and ranks of coals and the acetic acid is separated easily from the products of the reaction.

A one-gram sample of coal (60-mesh) was oxidized by a mixture of 25 ml. of concentrated nitric acid and 20 g. of sodium or potassium dichromate. Because of the corrosive action of the nitric acid, all-glass apparatus fitted with standard taper joints was used. The following pieces of apparatus were employed, 500-ml. round-bottom flask, connecting tube with dropping funnel, Hopkins spray trap, 105° elbow, 75° elbow turned down, condenser, adapter and receiver. The dichromate and coal sample were placed in the flask and the apparatus assembled. The nitric acid was then admitted through the dropping funnel. When the sample was a high rank coal the acid was added all at one time; when the sample was a low rank coal or an easily oxidized plant material such as cellulose, it was found advisable to dilute the nitric acid with an equal volume of water. Under these conditions, very little or no oxides of nitrogen were formed and the oxidation proceeded smoothly.

After all the nitric acid had been added and the first reaction had subsided, the mixture was refluxed gently. Certain coal samples foamed badly and with these it was necessary to heat slowly so that none of the sample was carried out of the oxidation flask. After refluxing for about half an hour, the mixture was distilled. Water was added through the dropping funnel as the distillation proceeded. The distillation was continued as long as acid was detected in the distillate. For most coals, 700 to 800 ml. was sufficient. Toward the end of the distillation bumping, at times, became severe; this was relieved by adding more nitric acid.

The amount of acetic acid was determined in the distillate as follows.[4,5] Excess potassium permanganate was added and the solution made alkaline to oxidize any of the lower oxides of nitrogen to nitrate ion. The solution was then made acidic to "alkacid" paper using sodium or potassium acid sulfate, and redistilled through a Hopkins spray trap. If the excess of permanganate was destroyed more was added. The acetic acid in the distillate was titrated with 0.1 N sodium hydroxide using phenolphthalein as the indicator. When only a slight excess of the acid sulfate was used, no difficulty was encountered with nitric acid distilling over since insufficient acid distilled, using the reagents alone, to turn methyl orange indicator from golden to

---

(1) Kinney, *Fuel*, **24**, 16 (1945).

(2) Horn, *Brennstoff-Chem.*, **10**, 362 (1929).

(3) Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 200 (1920).

(4) MacGregor, Evans and Hibbert, THIS JOURNAL, **66**, 41 (1944).

(5) Kuhn and L'Orsa, *Z. angew. Chem.*, **44**, 847–853 (1931).

pink. Using phenolphthalein less than 0.2 ml. of 0.1 *N* sodium hydroxide was required to develop a permanent pink color. Also, little or no carbonate ion was detected in the neutralized distillate when barium hydroxide was added. Distillation was continued until the acetic acid titre became small. The use of potassium salts has the advantage that the distillation can be carried further without the interference of salts crystallizing in the distilling flask. All yields of acetic acid are expressed as percentages on the dry, mineral matter-free basis, as are the yields of methane.

Test runs on samples of acetic acid gave titrations only 0.05 to 0.10 ml. of 0.1 *N* sodium hydroxide less than samples which had not been put through the oxidation procedure. Duplicate coal samples checked to less than 0.2%, numerical difference. The acetic acid in the neutralized distillate was identified as follows: The solution was evaporated to dryness, concentrated sulfuric acid and alcohol were added and the characteristic odor of ethyl acetate was easily detected. When the concentrated sulfuric acid was added only the odor of acetic acid could be identified, indicating an absence of higher acids such as butyric.

TABLE I

COMPARISON OF PERCENTAGES OF ACETIC ACID AND METHANE

Coal[a] no.	Vol. mat.	Acetic acid	Ratio of vol. mat. to acetic acid	CH_4 calcd.	CH_4 500°	CH_4[c] 1000°	CH_4 assumed from acetic acid structure
23	17.6	8.64	2.04	2.30	2.34	5.42	42.3
41	18.7	9.09	2.06	2.42	2.75	5.89	41.1
75	17.8	9.23	1.93	2.46	2.68	5.85	42.1
56	18.2	9.50	1.91	2.53	2.98	5.97	42.4
50	18.2	10.06	1.81	2.68	2.66	6.00	44.7
47	18.7	10.54	1.77	2.82	3.18	6.20	45.5
55	23.0	10.59	2.17	2.83	2.78	6.48	43.7
33	37.9	10.68	3.55	2.85	2.77	7.29	39.1
58	23.7	11.15	2.13	2.98	2.86	6.73	44.2
26	21.2	11.17	1.90	2.98	2.90	6.96	42.9
13	37.9	11.92	3.18	3.18	2.55	7.64	41.7
8	32.9	11.94	2.76	3.19	2.90	7.72	41.3
43	36.4	11.99	3.04	3.20	2.86	7.96	40.2
64	23.2	12.07	1.92	3.22	3.24	7.18	44.9
44	32.6	12.24	2.66	3.27	3.30	7.83	41.8
18	35.1	12.34	2.84	3.30	3.06	7.77	42.5
67	37.0	12.48	2.96	3.33	2.83	8.08	41.1
2	37.4	12.51	2.99	3.34	3.55	7.70	43.4
10	40.5	12.57	3.22	3.35	2.55	6.96	48.1
15[b]	33.8	12.84	2.63	3.43	3.10	8.01	42.8
14	38.4	12.91	2.97	3.44	2.80	7.63	45.1
27	26.8	12.95	2.07	3.46	3.41	7.71	44.9
40	37.9	13.08	2.90	3.49	2.98	7.75	45.0
39	41.1	13.12	3.13	3.50	2.82	8.12	43.2
54	41.2	13.23	3.11	3.53	2.71	7.39	47.8
16	41.1	13.24	3.10	3.53	2.65	8.03	44.0
22	40.5	13.28	3.05	3.54	3.25	7.78	45.6
45	40.9	13.29	3.08	3.54	3.46	7.00	50.6
68	38.2	13.36	2.86	3.56	2.95	7.26	49.0
46	34.9	13.38	2.61	3.57	2.92	7.12	50.1
36	39.1	13.57	2.88	3.62	3.02	7.84	46.2
53	34.8	13.81	2.52	3.68	2.96	7.34	50.2
28	36.8	13.89	2.65	3.71	3.22	8.06	46.0
72	37.7	14.12	2.67	3.77	3.23	7.99	47.2
19	41.3	14.85	2.78	3.96	2.89	8.34	47.5
66	40.1	15.23	2.63	4.07	3.49	9.58	42.5
65	32.8	15.76	2.08	4.20	3.46	8.35	50.3

[a] U. S. Bureau of Mines designation. [b] No. 2 Gas Bed coal, but not from the same mine as the Bureau of Mines sample. [c] Maximum yield of CH_4, 900° in some cases.

Discussion

It was established first that the acetic acid yielding structures are largely destroyed by carbonizing temperatures of 500°. This is shown in Fig. 1 for an Upper Freeport high volatile A bituminous coal mined in Indiana County, Pennsylvania. Since as much of the methane is evolved from a coal above 500° as below, it is apparent that this part of the methane must be split out of structures which do not yield acetic acid on oxidation.

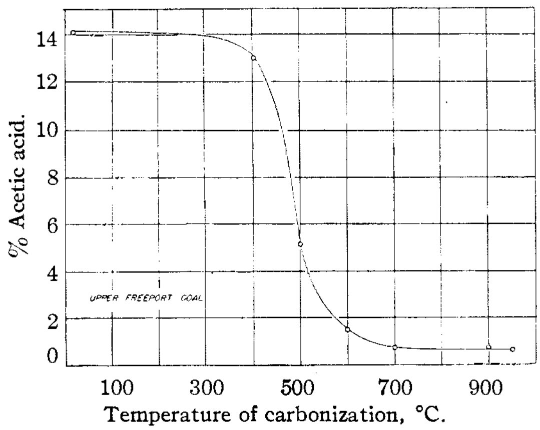

Fig. 1.

This was verified further by comparing the yields of acetic acid and methane from 37 of the coals used by the Bureau of Mines in their study of the carbonizing properties of American coals.[6] The coals are arranged in Table I according to increasing percentages of acetic acid. The coal numbers are those used by the Bureau of Mines to designate their samples. In general, the volatile matter content of the coals increases with the yield of acetic acid. Above about 12% acetic acid the coals are almost entirely high volatile coals and the correlation with per cent. volatile is fairly good as shown by the ratios of per cent. volatile matter to per cent. acetic acid. On the other hand, there is still better correlation with the yield of methane. The correlation is observed more easily if the comparison is made on the same basis, and for this purpose the per cent. of acetic acid was converted to per cent. methane,

---

(6) Davids, *et al.*, U. S. Bureau of Mines Technical Paper 655 (1943), bibliography p. 44.

column five, on a mole-for-mole basis. The percentage yields of methane calculated from the Bureau of Mines data at 500° are given in column six.

The best agreement between yield of acetic acid and yield of methane was obtained for coals yielding up to about 13.0% acetic acid. Above this point greater divergence was observed. Although the yield of methane obtained at 500° for a number of coals disagrees with the calculated yield, it is interesting to note that coals 33, 64 and 27, which are particularly out-of-place based on the per cent. of volatile matter, give good checks. Since the per cent of acetic acid can be obtained with considerable precision, it seems probable that a part of the discrepancies are due to the experimental difficulties in obtaining precise carbonization data at an intermediate temperature, such as 500°. Without doubt the data on the maximum yields of methane are more reliable and, if true, less variation would be expected between these values and the yields of acetic acid.

The maximum yields of methane are given in the seventh column in Table I. For most coals the temperature at which the maximum was obtained was 1000°. For comparison, the per cent. of the maximum yield of methane which may be assumed to come from the acetic acid-yielding structures, on a mole-for-mole relationship, is given in the eighth column. The percentages range from 39.1% for coal 33 to 50.6% for coal 45. Over two-thirds of the coals fall within a range of 5%, 41 to 46%, while the average is 44.6%. Consequently, it appears that the yield of acetic acid obtained from a coal is a fairly good indication of the yield of methane to be expected at 500° or 45% of the yield at 1000°, provided that the difference in molecular weights is taken into account.

The degree of correlation observed is all the more remarkable considering that several years elapsed between the time samples were collected for the carbonization studies and the present work. This correlation together with the observation that a carbonizing temperature of 500° largely destroys the acetic acid-yielding structures while a little less than half of the methane is evolved at this temperature, clearly demonstrates that there are two sources of methane on carbonization. One of these yields acetic acid on oxidation and is largely decomposed at temperatures between 400 and 500°, temperatures which produce profound changes in the chemical properties of all coals up to but not including the anthracitic coals. The second methane-yielding structure does not yield acetic acid on oxidation and is decomposed to methane at temperatures essentially above 500°. This indicates a more stable grouping, such as the methylene group, while possibly methyl groups constitute, for the most part, the first source of methane.

In a coal containing 5% hydrogen and yielding 15% acetic acid, 15% of the hydrogen is present as methyl groups. If the coal yields 8% methane on carbonization, 40% of the hydrogen is expelled as methane. Additional methyl groups are expelled in the form of methylated aromatics which would still further increase the quantity. Since such a large proportion of the hydrogen is involved in these groups it appears probable that, during the formation of coal, hydrogen atoms shift toward the outside of the coal molecules forming methyl and other alkyl groups, permitting the inner carbon atoms to assume the denser arrangement of aromatic or quinoidal structures or even groups of amorphous or graphitic carbon atoms.[7] All of which would be favored by earth pressures acting for geologic ages on the coal.

The acetic acid numbers of several coals which are not included in Table I appear in Table II.

TABLE II

ACETIC ACID FROM WESTERN COALS

Coals	% Volatile	% Acetic acid
High volatile bituminous		
Michigan, Swan Creek	40.4	13.5
New Mexico, Dawson (Blossburg)	42.6	18.9
Missouri, Bevier	43.9	16.6
Wyoming, No. 1	44.0	14.5
No. 3	44.2	14.4
Iowa, Mystic	45.0	15.3
Illinois, No. 2	47.0	14.7
Utah, Castle Gate "A"	47.9	16.5
Third Subseam	48.0	16.8
Castle Gate "A"	48.9	16.2
Subbituminous		
Wyoming, Monarch[a]	46.5	11.3
Lignitic		
North Dakota, Velva[a]	42.5	8.0
Texas, Alba	49.6	11.0

[a] Kindly furnished by Mr. J. D. Davis, U. S. Bureau of Mines, Pittsburgh, Pa.

For the most part these are Western coals of lower rank. Many of the high volatile bituminous rank coals of Western origin have higher acid numbers than similar coals from the Appalachian area. In this connection, it should be pointed out that the last three coals in Table I which have the highest acid numbers, are also Western coals from Utah and Washington. The subbituminous and lignitic coals in Table II have lower acid numbers. This would be expected on the basis that these fuels contain oxygen, which in the higher rank fuels has been eliminated to a greater extent, and to a lesser shift of the hydrogen into the methyl groups characteristic of the higher rank coals. The low yield from the North Dakota lignite indicates the unusual character of this coal and, as would be predicted from the correlation

---

(7) Hofmann, *Naturwissenschaften*, **32**, 260–268 (1944).

between methane and acetic acid numbers, has a low methane number of 4.69 at 910°,[8] which is about 60% of the average of the 37 coals in Table I.

With decreasing volatile matter content, the acetic acid number of coals, as well as the methane number, decreases. This is shown in Table III. From the results on Pennsylvania anthracite, it appears that true authracites have acid numbers of less than 2.0. As the volatile increases above 8.0% at the west end of the middle and southern anthracite fields the acid number rises above 3.0. Samples of semianthracite from Sullivan County, Pennsylvania, and Montgomery County, Virginia, with higher volatile matter gave higher acid numbers. Apparently semianthracites have acid numbers ranging from 3.0 to 7.0 while low-volatile bituminous coals have acid values from 8.0 to 11.0. From the data in Table I, medium-volatile coals range from about 10.0 to 13.0 and high-volatile coals from about 12.0 to as high as 18.9 in Table II. Thus, the acetic acid yielding structures appear to be most highly developed in the high-volatile rank coals since the lower rank fuels have somewhat lower numbers. Obviously acetic acid numbers could be used as a basis for classifying coals and would indicate the relative amount of a certain type of structure in coals. This is particularly noteworthy with the North Dakota lignite which has properties not suggested by its volatile matter content.

TABLE III

ACETIC ACID FROM HIGH RANK COALS

Coals	% Volatile	% Acetic acid
Anthracite		
Pennsylvania, Eastern Middle Field	3.6	1.0
Southern	5.0	1.5
Western Middle	5.3	1.8
Northern	5.6	1.5
Semianthracite		
Pennsylvania, Shamokin	8.3	4.6
Williamstown	8.7	3.3
"B" Seam, Mildred	8.8	5.1
Virginia, Brush Mountain Seam, McCoy	12.4	6.7
Low-Volatile Bituminous		
W. Va., Pocahontas No. 3, Killarney		16.8
Pennsylvania, Lycoming County	17.1	10.1
W. Va., Pocahontas No. 4, Coalwood	17.6	8.6
No. 3, Stephanson	18.2	9.5

In Table IV are given the acetic acid numbers of the petrographic constituents of several coals. In each case the woody or vitrain sample gave less acid than the attrital or the whole coal. Since the woody samples have retained more of the original cellular structure it is possible that they contain a greater amount of coalified cellulose and other carbohydrate material than the remainder of the coal in which coalified humus, lignin, resins and other more resistant plant products would be concentrated. If this is true the former should have a lower acetic acid number since it would not be expected *a priori* that coal formed directly from carbohydrate material would yield appreciable amounts of acetic acid on oxidation.

TABLE IV

ACETIC ACID FROM PETROGRAPHIC COMPONENTS OF COALS

Component	% Volatile	% Acetic acid
Washington Brown Coal		
Wood	75.5	1.3
Attritus	65.8	4.5
German Brown Coal		
Wood	65.5	4.0
Attritus	61.4	9.6
Oregon, Coos County		
Fungus decayed wood	49.5	4.9
Attritus	44.8	11.3
Illinois No. 6		
Vitrain	36.1	5.4
Whole coal	40.5	12.6
Utah, Blind Canyon		
Resin, benzene soluble	..	28.2

Furthermore a sample of coal oleo-resin taken from a Utah coal gave a high yield of acetic acid. It is not certain what yield would be obtained from the gum-resin types found in the older coals of the Appalachian region, but the relatively small amounts of these constituents in most coals make them of lesser importance. The data in Table IV shows the same trend as in Table II for the low rank fuels to increase in acetic acid-yielding structures as the rank increases up to the high volatile bituminous Illinois coal.

Since the woody constituents in Table IV gave smaller yields of acetic acid than the attrital coal, the plant products listed in Table V were subjected to the oxidation procedure. The carbohydrates, sucrose and cellulose gave low yields of acid as would be expected. Lignin samples gave somewhat larger yields which appeared to vary with the method of extraction. However, the quantity obtained, with the possible exception of the alkali-lignin samples, is insufficient to account for the acetic acid yielding structures in coals. Alkali-lignin appears to be a better source than acid- or neutral-lignin; but, since conditions are decidedly acidic in a peat bog, the alkali–lignin structure would not be expected to be formed. If this is correct, it may be that lignin is not as important as a source material from which coal is

---

(8) Calculated from Babcock and Odell's data, U. S. Bur. Mines Bull., **221**, 19 (1923).

TABLE V

ACETIC ACID FROM PLANT PRODUCTS

Substance	% Methoxyl	% Acetic acid
Sucrose		0.7
Cellulose, Cotton		1.6
Wood,[a] 98.8% cellulose		1.1
Lignin,[b] Acid		
Beech-HCl	19.9	1.6
Maple-HCl	21.3	1.7
Spruce-HCl-phenol	11.0	1.9
Spruce-HCl	15.5	2.2
Neutral		
Spruce-dioxane	11.2	2.4
Spruce-phenol	10.3	2.4
Alkali		
Hardwood ("Meadol")		4.1
Jack Pine	14.8	4.3
Spruce	14.5	4.9
Commercial kraft	12.5	10.3
Wood,[b] Canadian Black Spruce		3.5
Extd. benzene–alcohol (1:1)	4.8	3.6
Ground Pine, whole plant		3.7

[a] Black gum wood cellulose, kindly furnished by Dr. Fred Olsen, Western Cartridge Co., East Alton, Illinois. [b] Lignin and wood samples were supplied through the cooperation of Dr. F. E. Brauns, The Institute of Paper Chemistry, Appleton, Wisconsin.

TABLE VI

ACETIC ACID FROM HUMIC COMPOUNDS

Source	Solubility in alkali	% Acetic acid
Sucrose, No. 1	Soluble	15.5
No. 2[a]	Soluble	15.8
	Insoluble	14.8
Glucose[a]	Soluble	18.5
	Insoluble	2.7

[a] Samples kindly supplied by Dr. Harold Hibbert, see ref. 10.

made as the Fischer–Schrader theory[9] requires. There remains, however, the possibility that the lignin structure is altered during coalification so as to yield more acetic acid on oxidation. The yield of acid from the samples of wood in Table V indicate that native lignin has no unusual properties.

Considerable evidence has been accumulated to the effect that the conversion of plant remains into peat involves the formation of humic compounds, among which the humic acids have been studied most extensively. Since humic acid-like compounds, more or less indistinguishable from natural humic acids, have been produced from carbohydrates[10,11] in addition to many other carbonaceous materials[12–18] it seems quite possible that a part of the humic compounds formed in a peat deposit come from the carbohydrates of the plant remains. Consequently, synthetic humic acids prepared from glucose and sucrose[10] were oxidized and the results compared in Table VI. The yields are more nearly comparable to those obtained from the bituminous coals than any other source material investigated, excepting the Utah coal resin. These results, together with the observation that synthetic carbohydrate humic acids yield methane on carbonization,[3] strongly indicate the importance of this type of material in the formation of coal. In view of this information, it seems likely that the woody samples in Table III have a low acid number because the wood was preserved in the peat stage without the chemical conversion which accompanies the formation of humic matter. It also seems likely that the attrital portions of these coals were partly formed from humic matter resulting from carbohydrates of the plant remains.

Since the synthetic humic acids, as well as natural acids and lignin, are thought to contain phenolic hydroxyl groups,[19,20] several phenolic derivatives have been oxidized and the results given in Table VII. Only those phenols in which methyl groups are attached directly to the aromatic nucleus, yield appreciable quantities of acetic acid. From this it would appear that acetic acid is not formed in any quantity from the basic phenolic structure itself, but that ring-methylated, or possibly alkylated, phenols are susceptible. Since lignin contains a three-carbon side chain which may undergo reduction during coalification it may be an important source of the acetic acid obtained from coal. Consequently, additional data are needed to prove that cellulose be excluded as source material of coal.

TABLE VII

ACETIC ACID FROM PHENOLS

Substance	% Acetic acid
o-Cresol	32.3
m-Cresol	32.0
p-Cresol	27.4
Eugenol	2.5
Phenol	1.9
Vanillin	1.0

Several coals and shales rich in spores and algae have also been oxidized and the results assembled in Table VIII. The lower yield of acetic acid from these samples indicates that spore and algae remains yield less acid than the more usual plant constituents of coal. Very likely a large part of these coals and shales is made up of humified and coalified plant materials which give normal yields of acetic acid. Therefore, it seems possible that

---

(9) Fischer and Schrader, *Brennstoff-Chem.*, **2**, 37–45 (1921).

(10) Plunguian and Hibbert, THIS JOURNAL, **57**, 528 (1935).

(11) Jodl, *Brennstoff-Chem.*, **22**, 157, 217 (1941).

(12) Eller, *ibid.*, **2**, 129 (1921).

(13) Marcusson, *Ber.*, **54**, 542 (1921).

(14) Gortner and Norris, THIS JOURNAL, **45**, 550 (1923).

(15) Orlov and Tischenko, *J. Appl. Chem.*, *U. S. S. R.*, **6**, 112 (1933).

(16) Biggs, THIS JOURNAL, **58**, 1020 (1936).

(17) Charmbury, *et al.*, *ibid.*, **67**, 625 (1945).

(18) Hamdi, *Kolloid-Beihefte*, **54**, 554 (1943).

(19) Fuchs and Sandhoff, *Fuel*, **19**, 45–48, 69–72 (1940).

(20) Ubaldini, *Brennstoff-Chem.*, **18**, 273 (1937).

TABLE VIII

ACETIC ACID FROM OTHER COAL TYPES[a]

Sample	Ash %	Volatile %	Acetic acid %
Penna. Spore Cannel	45.5	28.6	12.6
Michigan Shaly Spore Coal	48.0	25.9	10.2
Michigan Splint under Spore Coal	4.3	37.9	8.8
Utah Cannel, Kane County	19.0	54.7	10.5
Australian Coorongite	..	..	7.6
Penna. Boghead Cannel	45.0	30.1	12.9
Colorado Oil Shale	58.9	38.9	12.8
Wyoming Oil Shale	55.2	45.9	14.4

[a] Samples obtained through the courtesy of Dr. James Schopf, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

the process of humification and preservation of spores and algae resulted in a product which is similar to that made from other plant materials.

Summary

The quantitative oxidation of coal to acetic acid shows that: (1) The structures in coal which yield acetic acid on oxidation are largely decomposed by carbonizing temperatures of 500°. (2) The yield of acetic acid from bituminous coals bears a direct relationship to the amount of methane produced on carbonization. (3) High rank coals give less acetic acid, the amount diminishing with the volatile matter content. (4) Woody portions of low rank coals give less acetic acid than the attrital portion. (5) High yields of acetic acid from synthetic carbohydrate-humic acids indicate that carbohydrates may have been an important factor in the formation of coals as well as lignin.

STATE COLLEGE, PENNSYLVANIA

RECEIVED AUGUST 19, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Studies on the Mechanism of the Cannizzaro Reaction[1]

BY ELLIOT R. ALEXANDER[2]

Recently the Cannizzaro reaction[3] has been the subject of careful kinetic analysis.[4] It now appears quite certain that in the case of substituted benzaldehydes at least,[5] the reaction rate may be represented by the equation

$$\text{rate} = k(\text{ArCHO})^2(\text{OH}^-)$$

in aqueous dioxane, pure methanol and aqueous methanol.[4,6] Since no unusual precautions were taken to exclude oxygen in carrying out the reaction, this general agreement among the different investigators suggests that the reaction proceeds by an ionic rather than radical mechanism. Also the fact that electron attracting substituents in the aromatic nucleus facilitate the reaction while electron repelling groups inhibit the reaction[3] implies the formation of ionic intermediates. It has been proposed, however, that a chain or free radical mechanism is involved[7] and there is indeed some evidence to support this view. Thus, some unpublished experiments of Weiss[8] indicate that under suitable conditions the reaction is accelerated by the presence of ferrate, silver oxide, or benzoyl peroxide and that it is inhibited by ferrous or manganous hydroxide. Furthermore, it has been shown by Kharasch and Foy[9] and confirmed by Urushibara and Takebayashi[10] that the yield of the heterogeneous reaction is lowered considerably or that the reaction is even inhibited completely by employing peroxide-free aldehyde.

Accordingly, it was the purpose of this investigation to study the Cannizzaro reaction with benzaldehyde in a homogeneous medium under peroxide-free conditions and also in the presence of added peroxides or peroxide inhibitors.

In Fig. 1 are summarized the data obtained by carrying out the reaction according to the procedure developed by Molt[6a] with carefully purified reagents under an atmosphere of nitrogen. The experiments were conducted at 100° in 74% aqueous methanol and the course of the reaction was followed by titrating the disappearance of alkali. Under these conditions, Molt and others[6] have shown that the transformation $2\text{ArCHO} + \text{NaOH} \rightarrow \text{ArCH}_2\text{OH} + \text{ArCOONa}$ is almost quantitative, and that the disappearance of alkali from the reaction mixture represents a measure of the extent of reaction. Runs were made with benzaldehyde alone and with benzaldehyde in the presence of one molar per cent of

---

[1] Presented before the Division of Organic Chemistry at the 110th meeting of the American Chemical Society, Chicago, Illinois, September, 1946.

[2] Frank B. Jewett Fellow. Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

[3] An excellent review of the Cannizzaro reaction has been published by T. A. Geissman, "Organic Reactions," Vol. II. John Wiley and Sons, Inc., New York, N. Y., 1944, p. 94.

[4] Tommila, *Ann. Acad. Sci. Fennicae, Ser.*, **A59**, No. 8, 3 (1942); *C. A.*, **38**, 6175 (1944).

[5] Paul, *J. Gen. Chem. U. S. S. R.*, **11**, 1121 (1941); *C. A.*, **37**, 3733 (1943), has found that the order of the Cannizzaro reaction with formaldehyde depends upon the concentration of the reactants employed.

[6] (a) Molt, *Rec. trav. chim.*, **56**, 233 (1937); (b) Blanksma and Zaaijir, *ibid.*, **57**, 727 (1938); (c) Lock and Eitel, *Monatsh.*, **72**, 392 (1939).

[7] Weiss, *Trans. Faraday Soc.*, **37**, 782 (1941).

[8] Weiss, *ibid.*, 786 (1941).

[9] Kharasch and Foy, THIS JOURNAL, **57**, 1510 (1935).

[10] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **12**, 328 (1937).