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Abstract

Full Text

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CHEMISTRY

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ON THE PRODUCTS OF OXIDATIVE DEGRADATION OF HUMIC ACIDS

(Presented by Academician M. M. Shemyakin, 10 February 1965)

The oxidative degradation of the organic matter of fossil coals during weathering proceeds through a series of stages and leads to the accumulation of humic acids in the seams. Experiments on the artificial oxidation of humic acids have shown ([1,2]) that their further degradation is accompanied by the formation of low-molecular-weight organic acids (acetic, oxalic, benzenecarboxylic acids). Owing to the ready solubility of these products in water, their accumulation under natural conditions usually does not occur. A different situation should obtain in northern latitudes, where permafrost is widespread and there is no movement of groundwater. Indeed, we have found the presence of significant amounts (up to 10% and more) of water-soluble organic acids in weathered coals from a number of deposits in the North-East of the USSR ([3,4]). Among these acids there were identified acetic, propionic, oxalic, succinic, and benzenecarboxylic acids with 2–5 carboxyl groups.

In the present work it is shown that, along with carboxylic acids, under the indicated conditions aromatic oxy acids are formed, and their amount, judging from the results of methylation with dimethyl sulfate, reaches 50% of the water-soluble fractions of weathered coal. Consequently, the direction of oxidative destruction of humic matter during natural weathering differs substantially from that in experiments on the artificial oxidation of coals by various oxidizing agents, where the formation of appreciable amounts of aromatic oxy acids was not established.

The mild conditions of long-term weathering, which proceeded under conditions of negative temperatures, make it possible to regard the isolated acids

Table 1

Amount of isolated individual acids

Carboxylic acids	Yield in % of the water-soluble fraction	Oxycarboxylic acids	Yield in % of the water-soluble fraction
Oxalic	6	4-Oxybenzoldicarboxylic-1,3	3
Succinic	8	4-Oxy, 5-methylbenzoldicarboxylic-1,3	0.5
Adipic	2	Dioxybenzoldicarboxylic	0.5
Benzenedicarboxylic-1,2	4	5-Oxybenzoltricarboxylic-1,2,4	3
Benzenedicarboxylic-1,3	0.5	2-Oxybenzoltricarboxylic-1,3,5	1
Benzenedicarboxylic-1,4	0.5	4-Oxy, 6-methylbenzoltricarboxylic-1,2,3	0.5
Benzenetricarboxylic-1,2,3	0.5	5-Oxybenzoltetracarboxylic-1,2,3,4	2
Benzenetricarboxylic-1,2,4	5		
Benzenetetracarboxylic-1,2,3,4	1		
Benzenetetracarboxylic-1,2,4,5	4		

as primary products of the decomposition of the coal substance. From this point of view it is of interest to note the presence of oxy acids with a methyl group on the nucleus and the predominance of compounds with 3 and 4 carboxyl groups. Six individual oxy acids were isolated (see Table 1); in addition, the presence of dioxyphthalic acids and acids containing a methoxy group was noted. The primary character of these latter, however, requires confirmation.

Table 1 gives data characterizing the yields of individual acids; the figures relating to oxy acids are underestimated owing to losses during their separation from the carboxylic acids.

Experimental Part

Weathered coal from the Kadykchan deposit (Magadan Region) was exhaustively extracted with hot water; 6.3% of a dark-brown substance passed into solution, consisting of free organic acids and their iron and aluminum salts (ash content 20%). The extract was acidified with sulfuric acid and extracted with methyl ethyl ketone. On methylation with dimethyl sulfate in a strongly alkaline medium the mixture of acids gave a product containing 7.5% OCH_3, which corresponds to a content of about 50% oxy acids (calculated as monooxy compounds). Esterification of the acids by prolonged heating with methanol containing a mineral acid gave 4.8% neutral esters, 1.6% acidic esters, and 0.5% resinous residue (based on the original coal). The neutral esters were distilled in vacuo, and the fractions obtained were studied in detail (Table 2).

Table 2

Composition of the methyl ester fractions

Boiling point, °C and pressure (mm Hg)	Fraction yield, %	Molecular weight	C %	H %	OCH_3 %	Acid equivalent weight
up to 170/760	3.8	–	40.8	5.1	51.1	46.1
170–220/760	15.1	141	44.4	7.4	37.6	65.1
75–120/2–3	3.2	175	48.9	7.7	31.9	82.8
120–170/2–3	11.9	195	50.5	5.9	29.7	88.9
170–190/2–3	7.8	247	56.5	5.1	31.9	82.5
190–200/2–3	10.8	255	56.1	5.0	32.7	84.6
200–215/2–3	8.2	263	55.4	4.9	32.2	80.5
215–230/2–3	10.9	284	55.4	4.9	32.4	78.5
230–252/2–3	4.0	286	55.7	4.7	30.1	79.2
residue	18.1	–	59.4	5.4	–	–

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The isolation of individual acids from the fractions (except for the first three) was achieved by partition chromatography on silica gel in various systems, of which the best results were given by the systems benzene—acetone, benzene—dioxane, and chloroform—butanol, saturated with aqueous acetic acid (1 : 1).

Identification of the isolated acids was carried out by comparing their IR spectra with the spectra of synthetic preparations. The spectra were recorded in KBr on a UR-10 instrument. In individual cases the structures of the acids were confirmed by NMR spectra recorded on a JNM-C-60; tetramethylsilane served as internal standard, and deuteromethanol as solvent. All melting points are uncorrected.

After one crystallization the first fraction gave pure dimethyl oxalate with m.p. 54.2°. The second fraction consisted of esters of oxalic and succinic acids. A small amount of adipic acid with m.p. 151.5—152° was also isolated. Fraction 3 contained esters of phthalic acids (*o*-, *m*-, *p*-) with predominance of the ortho isomer.

In fraction 4, in addition to phthalic acids, acids were found that were sparingly soluble in hot water and gave a violet-red coloration with $FeCl_3$. Two substances were isolated:

4-Oxyisophthalic acid, m.p. 308-310° (with decomposition).

Found, %:	C 52.81, 53.04;	H 3.20, 3.22
$C_8H_6O_5$. Calculated, %:	C 52.75;	H 3.32.

Its dimethyl ester: m.p. 94-95°; equiv. wt. (by saponification number) 105.4.

Found, %:	C 57.17, 57.02;	H 4.55, 4.66
$C_{10}H_{10}O_5$. Calculated, %:	C 57.14;	H 4.80

4-Oxy-5-methylisophthalic acid; i.r. spectrum: 460, 683, 927, 970, 1222, 1285, 1381, 1408, 1460, 1568, 1665, 1710, 2500-3200 cm^{-1}. M.p. 295°; equiv. wt. 97.8.

Found, %:	C 54.78, 54.86;	H 4.16, 4.22
$C_9H_8O_5$. Calculated, %:	C 55.07;	H 4.11.

Lit. ([5]): m.p. 295-298°; equiv. wt. 98.1.
Its dimethyl ester: m.p. 128-130°

Found, %:	C 58.65;	H 5.37
$C_{11}H_{12}O_5$. Calculated, %:	C 58.92;	H 5.39.

Lit. ([6]): m.p. 128-132°.

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Fractions 5 and 6 consisted of triacid carboxylic and hydroxycarboxylic acids. The presence of hemimellitic acid and of large amounts of trimellitic acid was shown.

Among the hydroxy acids, the following were established: **5-oxybenzoltricarboxylic-1,2,4-acid**; i.r. spectrum: 760, 1222, 1299, 1308, 1410, 1453, 1504, 1687, 1715, 2500–3200 cm^{-1}.

N.m.r. spectrum: two signals at 7.05 and 8.35 ppm, corresponding, respectively, to the hydrogens in positions 6 and 3. M.p. 238–240°; equiv. wt. 75.9.

Found, %: C 47.76, 47.78; H 2.84, 2.84
$C_9H_6O_7$. Calculated, %: C 47.80; H 2.68.

Its trimethyl ester ($CH_3OH + HCl$): m.p. 64°.

Found, %: C 54.03; 53.82; H 4.66, 4.62; OCH_3 33.9
$C_{12}H_{12}O_7$. Calculated, %: C 53.73; H 4.51; OCH_3 34.7

Methoxytrimethyl ester (diazomethane): m.p. 62–62.5°

Found, %: C 55.48; H 4.99; OCH_3 43.0
$C_{13}H_{14}O_7$. Calculated, %: C 55.23; H 4.99; $4\,OCH_3$ 44.0.

Lit. (^{7}): m.p. 62–63°.

2-Oxybenzoltricarboxylic-1,3,5-acid; i.r. spectrum: 645, 690, 906, 1110, 1188, 1240, 1365, 1404, 1433, 1485, 1600, 1700–1720, 2500–3200, 3335 cm^{-1}. M.p. 309–310°; equiv. wt. 75.9.

Found, %: C 47.80, 47.62; H 2.69, 2.73.

Lit. (^{8}): m.p. 86°.

From fraction 7, in addition, a small amount of a tribasic hydroxy acid was isolated, subliming above 140–150°. M.p. 224–225°; equiv. wt. 80.6; H_{act} 1.64%.

Found, %: C 49.82; H 3.51
$C_{10}H_8O_7$. Calculated, %: C 50.01; H 3.36; $4H_{act}$ 1.66. Equiv. wt. 80.0

The trimethyl ester melted at 135–136°.

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The substance corresponds to 4-hydroxy-6-methylbenzene-1,2,3-tricarboxylic acid (cochenillic acid), which sublimes at 145–170°, m.p. 224–225° (9), m.p. of the trimethyl ester 136–138° (10). Fractions 8-9 contained mainly esters of benzene-1,2,3,4- and -1,2,4,5-tetracarboxylic acids.

From fraction 9 there was also isolated a hydroxy acid which gave a red-brown coloration with $FeCl_3$ and had m.p. 241–243°*; equiv. wt. 67.7.

IR spectrum: 500, 645, 890, 910, 1223, 1270, 1402, 1474, 1580, 1690–1730, 2500–3200 cm^{-1}.

NMR spectrum: a signal at 7.35 m.d., corresponding to hydrogen of the benzene ring situated between COOH and OH groups.

Found, %:	C 44.80, 44.73;	H 2.30, 2.31
$C_{10}H_6O_9$. Calculated, %:	C 44.45;	H 2.23. Equiv. wt. 67.5

Methoxytetramethyl ester (diazomethane): m.p. 127.5–128.5°.

Found, %:	C 52.90, 53.10;	H 4.88, 4.95;	OCH_3 43.4
$C_{15}H_{16}O_9$. Calculated, %:	C 52.94;	H 4.75;	$5OCH_3$ 45.6

Mixed melting points both of the acid and of the methoxytetramethyl ester with synthetic preparations showed no depression.

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* Dimroth gives for 5-hydroxybenzene-1,2,3,4-tetracarboxylic acid m.p. 212–214° (11).

Note: Figure translations are in progress. See original paper for figures.

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