PERSULFATE OXIDATION OF HUMIC ACIDS EXTRACTED FROM THREE DIFFERENT SOILS

F. MARTIN and F. J. GONZALEZ-VILA

Centro de Edafología y Biología Aplicada del Cuarto, Consejo Superior de Investigaciones Científicas,
Aptdo. 1052, Sevilla, Spain

Summary—Three soil humic acids were degraded by a new mild chemical oxidation method using potassium persulfate at pH 2.0. The method degraded 30–40% of the starting material. The type and relative quantities of the products or fragments released as determined by GC/MS varied with the source of the polymers. Humic acid extracted from an Inceptisol yielded fatty, benzenecarboxylic and phenolic acids; humic acid from a Typic Chromoxerert produced largely dialkyl phthalates, and humic acid from an Humic Haplorthod gave only branched and straight-chain fatty acids. It is suggested that the method may be used to advantage as a first oxidant in a sequential degradation.

INTRODUCTION

Oxidative degradation methods have been frequently and successfully used to characterize humic substances (Hayes and Swift, 1978; Schnitzer, 1977). Partial degradation with solutions of potassium permanganate of a large number of humic acids from soils, waters and sediments have yielded aliphatic, phenolic and benzenecarboxylic acids as major fragments (Schnitzer and Khan, 1972; Rashid and King, 1970; Gjessing, 1976).

Alkaline solutions of cupric, mercuric and silver oxides have also been used to degrade humic substances, but only the first has been widely applied. It also yields aliphatic, phenolic and benzenecarboxylic acids but the relative amounts are not the same as for potassium permanganate oxidation (Schnitzer and Ortiz de Serra, 1973).

These two degradation methods are usually employed in alkaline conditions and produce a drastic breakdown of the structure, with the possibility of secondary reactions accelerated by the presence of O_2 .

The use of oxidants under acidic conditions has also been applied to humic substances. Meneghel *et al.* (1972) and Schnitzer and Skinner (1974), de-

scribed the use of peracetic acid but the percentage of original polymer degraded, the total yield of fragments and the types of structures identified were similar to those obtained with the permanganate and cupric oxide methods.

It may be worthwhile to investigate the use of other, less drastic reagents as a first step in a sequential oxidative degradation procedure using oxidants of increasing strength. Martin *et al.* (1981) have developed an oxidation method which is carried out under acid conditions and employs a new reagent, potassium persulfate, which is used by the oceanographers to determine carbon in seawater (Sharp, 1973) and which is a mild oxidant of humic substances.

In our work three humic acids from different soil types were oxidized with persulfate and the nature of the fragments or compounds released were identified.

MATERIALS AND METHODS

Origin and properties of humic acids

Some properties of the soils used are listed in Table 1. Methods of extraction, separation and purification of the samples and for ultimate and functional group

Table 1. Origins and some characteristics of soil samples

Sample	Horizon	Depth (cm)	Soil series	Order	Geographical origin	pH	% C
1	Surface	0–10	Coto Doñana	Inceptisols	Huelva (Spain)	3.4	6.4
2	Surface	0–20	Utrera	Typic Chromoxerert	Sevilla (Spain)	7.8	1.0
3	Bh	20–30	Ribadeo	Humic Haplorthod	Lugo (Spain)	3.3	6.6

Table 2. Analytical characteristics of humic acids

Sample	% (dry, ash free basis)					m-equiv g ⁻¹		
	C	H	N	O	Ash	Total acidity	Carboxyls	Phenolic hydroxyl
HA-1	57.1	4.5	3.4	35.0	1.1	6.0	3.3	2.7
HA-2	57.7	5.6	5.8	30.9	1.5	5.7	3.1	2.6
HA-2'	55.5	3.5	2.2	38.8	0.9	6.6	5.2	1.4
HA-3	59.4	4.2	3.3	33.1	0.7	10.5	4.2	6.4

HA-2' (humic acid extracted from sample 2 with a mixture of sodium pyrophosphate:sodium hydroxide 1:1).

Table 3. Persulfate oxidation products of HAs

Compounds identified	HA-1	HA-2	HA-2'	HA-3
(1) Dimethyl malonate			+	
(2) Dimethyl succinate	+		+	
(3) 3-methoxybenzoic acid methyl ester	+			
(4) Dimethyl glutarate	+		+	+
(5) 2,4-dimethyltridecanoic acid methyl ester				++
(6) 1,2-benzenedicarboxylic acid dimethyl ester	+	+		+
(7) 1,3-benzenedicarboxylic acid dimethyl ester		+		
(8) <i>n</i> -C ₁₃ fatty acid methyl		++	++	
(9) Diethyl phthalate		+	+	
(10) <i>n</i> -C ₁₄ fatty acid methyl ester	+	++	++	++
(11) 3,4-dimethoxybenzoic acid methyl ester	++			
(12) 2,3-dimethoxybenzoic acid methyl ester	+			
(13) 2,4-dimethyl pentadecanoic acid methyl ester				+++
(14) <i>n</i> -C ₁₅ fatty acid methyl ester				+
(15) Phthalate		+++	+++	
(16) 2,4-dimethyl hexadecanoic acid methyl ester				+++
(17) <i>n</i> -C ₁₆ fatty acid methyl ester	+++	+	+	++
(18) 2,4-dimethyl heptadecanoic acid methyl ester				+++
(19) Isobutyl phthalate	+	+++	+++	+
(20) 3-methoxy-1,2-benzenedicarboxylic acid dimethyl ester	+			
(21) 2-methoxy-1,5-benzenedicarboxylic acid dimethyl ester	+			
(22) 1,2,3-benzenetricarboxylic acid trimethyl ester	+			++
(23) 2,4-dimethyl octadecanoic acid methyl ester				+++
(24) <i>n</i> -C ₁₈ fatty acid methyl ester	+++	+	+	++
(25) 2,4-dimethyl nonadecanoic acid methyl ester				+
(26) Dibutyl phthalate	+	+++	+++	+
(27) 1,3,5-benzenetricarboxylic acid trimethyl ester	+			
(28) 3-methoxy-1,2,4-benzenetricarboxylic acid trimethyl ester	++			
(29) 2-methoxy-1,3,5-benzenetricarboxylic acid trimethyl ester	++			
(30) 1,2,3,4-benzenetetracarboxylic acid tetramethyl ester	++	+		
(31) 1,2,4,5-benzenetetracarboxylic acid tetramethyl ester	++			
(32) 5-methoxy-1,2,3,4-benzenetetracarboxylic acid tetramethyl ester	+			
(33) 2-methoxy-1,3,4,5-benzenetetracarboxylic acid tetramethyl ester	+			
(34) <i>n</i> -C ₂₂ fatty acid methyl ester			+	
(35) Di-(2-ethyl hexyl)phthalate	+	+++	+++	+
(36) Benzenepentacarboxylic acid pentamethyl ester	++			
(37) Methoxy-benzenepentacarboxylic acid pentamethyl ester	+			

+—Low content; ++—Medium content; +++—High content.

analyses have been described by Martin *et al.* (1977). Table 2 shows the elemental composition and functional group analyses of the humic acids.

Oxidation method

Humic acid (200 mg) was placed in a Teflon beaker with 25 ml water to which 50 ml of a 5% solution of potassium persulfate were added. The beaker was placed in a digestion bomb and heated with stirring at 140°C for 2 h. (The initial and final pH was in all cases 2.0 and 1.8 respectively). After cooling, the residue was separated by centrifugation and the liquid was extracted with ethyl acetate for 72 h in a liquid-liquid extractor. The extract was evaporated to dryness in a rotary evaporator, suspended in methanol and methylated with an excess of diazomethane. The residue after two successive oxidations accounted for 60–70% of the starting materials. All solvents were HPLC grade or twice glass distilled.

Gas chromatography-mass spectrometry (GC/MS)

The methylated degradation products were analysed by injection into a GC/MS computer system (Hewlett Packard model 5992 B). Separation took place in a 3000 by 3 mm stainless steel column packed with 3% OV-17 on Chromosorb W AW HMDS 80–100 mesh, programmed from 150° to 270°C at a rate of 4°C min⁻¹. Helium at a flow rate of 20 ml min⁻¹ was used as carrier gas. The chromatographic effluent was passed via a jet into the

mass spectrometer operated at an ionizing voltage of 70 eV.

The individual compounds were identified by comparison of their mass spectra with library reference spectra and in some cases with the GC retention time of pure compounds.

RESULTS

Table 3 shows the identified compounds after persulfate oxidation of the humic acids. Because the oxidation products were methylated prior to GC separation and MS identification, and in view of the low methoxyl content of the humic acids, it is likely that most of the carboxyl and hydroxyl groups occurred in the original materials as such rather than esters and ethers.

According to the peak heights and in decreasing order, the most abundant compounds identified from the HA-1 oxidation products were the *n*-fatty acids 17 and 24, followed by benzenecarboxylic acids 36, 30 and 31, and by phenolic compounds 28, 29 and 11. Dialkyl phthalate 19, 26 and 35 were present in small amounts. The remaining compounds were present in minor concentrations.

The most abundant compounds released by persulfate oxidation of HA-2 were the dialkyl phthalates 26, 19, 15 and 35 and the *n*-fatty acids 10 and 8. Benzenecarboxylic acids 5, 7 and 30 were only present in trace amounts.

HA-2' was extracted with a mixture of sodium pyrophosphate: sodium hydroxide from the same soil as HA-2 and was studied to observe the influence of the extractant. As noted in Table 3 the oxidation products were the same as those for HA-2 but benzenecarboxylic acids were absent. In addition smaller amounts of dicarboxylic acids and some other *n*-fatty acids were present. Also smaller amounts of methyl benzylsulphonate, dibenzylsulphoxide and *N,N*-dimethyl-*p*-toluensulphonamide, not shown in Table 3, were identified.

Major compounds identified from the HA-3 oxidation products were the branched fatty acids 18, 23, 16 and 13 followed by the *n*-fatty acids 17, 24 and 10 and the benzenecarboxylic acids 6 and 22. Minor compounds identified were the dialkyl phthalates 19, 26 and 35.

Methylation with diazomethane prior to oxidation with persulfate failed to increase the yield and nature of oxidation products, on the contrary some compounds were absent in the methylated substrates.

DISCUSSION

The compounds released by the persulfate oxidation of the three humic acids were different in nature and relative amounts of different compounds, though the degradation percentages were very similar. Whereas HA-1 gave the largest number of compounds and more types of structures, especially benzenecarboxylic, phenolic and fatty acids, HA-2 yielded almost exclusively dialkylphthalates and HA-3 produced largely branched and *n*-fatty acids. Compared to other oxidation methods, such as the permanganate or alkaline cupric oxide, the different humic acids showed not only differences in the aliphatic:phenolic:benzenecarboxylic acid ratios but also in the types of products released by the oxidation.

In the oxidation products of HA-2 small amounts of aromatic S-containing compounds were detected and though Neyroud and Schnitzer (1975) postulate that some S-containing compounds might be artifacts from reagents used to generate diazomethane, this oxidation was carried out with unmethylated substrate. Still a reaction between the persulfate and the humic acid cannot be excluded. For example, the oxidation of phenol with persulfate at a pH above 7.0 yields hydroxysulphonate in small amounts (Behrman, 1963) whereas the oxidation mechanism of phenolic compounds, under acidic conditions is not known.

Since early investigations of persulfate oxidation reactions there has been general agreement that the oxidizing species is the sulfate radical $\text{SO}_4^{\cdot -}$ or, in some cases, also the hydroxyl radical $\text{OH}^{\cdot}$ (Ebersson *et al.*, 1968). The reactions of organic compounds with persulfate are very slow at room temperature but at 80°C the reaction rate increases and the decomposition kinetics of the persulfate anion is:

Similarly to potassium permanganate and peracetic acid, the persulfate oxidation is an electron transfer reaction. However, as with the other oxidants the mechanism is very complex.

The premethylation of humic acids has been a common practice in degradation studies. The methylation stabilizes the phenolic groups against degradation and the yields and types of oxidation products increase compared with unmethylated substrate. As most of the degradation occurs under alkaline conditions, the methylation is convenient but with persulfate the phenols are more stable in acid medium.

Since soil humic acids appear to be highly cross-linked aromatic polymers of high molecular weight with covalent carbon-carbon-, ether- and ester-linkages connecting the substituted moieties (Schnitzer, 1977) or groups of similar structures aggregated by weak covalent and non-covalent bonds, (Wershaw *et al.*, 1977) persulfate possibly degrades the weaker bonds of such aggregates. One could conclude that our HA-1 is the least mature of the three humic acids studied and that a part of the phenolic and benzenecarboxylic acids are weakly bonded and consequently released by the persulfate.

HA-2 is a well polymerized humic acid (Martin *et al.*, 1971) and the compounds that form the building blocks (phenolic and benzenecarboxylic acids) might be very tightly bound. It is known that humic materials adsorb organic compounds such as dialkyl phthalates, thereby modifying their behaviour and activity by making them water soluble (Matsuda and Schnitzer, 1971). The adsorbed phthalates are released by persulfate. A blank run gave no phthalates.

HA-3 is a humic acid extracted from a podzolic soil and produces almost exclusively fatty acids both branched and straight-chain when oxidized by the persulfate procedure. The presence of fatty acids in humic substances from different origin has been shown by several authors but in most of the papers dealing with this subject a predominance of straight-chain fatty acids over branched chain has been found. However, upon persulfate oxidation HA-3 gives a ratio of branched to straight-chain close to unity.

Persulfate oxidation is a mild degradative method that allows the use of a sequence of degradative methods since the residues after the reaction constitute 60–70% of starting materials. It also demonstrates differences among humic acids since the nature and relative abundance of the oxidation products released by the mild oxidation vary greatly.

Acknowledgements—We thank Professor J. P. Martin of University of California, Riverside, for his critical review of this manuscript and Mrs T. Verdejo for technical assistance.

REFERENCES

- Behrman E. J. (1963) Studies on the mechanism of the Elbs peroxydisulfate oxidation. *Journal of the American Chemical Society* **85**, 3478–3482.
- Ebersson L., Granse S. and Olofsson B. (1968) Studies on the Kolbe electrolytic synthesis. IX. Comparison between anodic and peroxydisulfate oxidation of carboxylates: kinetics of peroxydisulfate decomposition in the presence of acetate ion. *Acta chemica scandinavica* **22**, 2462–2470.
- Gjessing E. T. (1976) *Physical and Chemical Characteristic of Aquatic Humus*. Ann Arbor, Michigan.
- Martin F., Díaz-Barrientos E. and González-García F. (1971) Constitución y propiedades de la materia húmica de una tierra negra andaluza. *Anales de edafología y agrobiología* **30**, 535–543.

- Martin F., Sáiz-Jiménez C. and Cert A. (1977) Pyrolysis gas chromatography-mass spectrometry of soil humic fractions. I. The low boiling point compounds. *Soil Science Society of America Journal* **41**, 1114-1118.
- Martin F., Sáiz-Jiménez C. and González-Vila F. J. (1981) The persulfate oxidation of a soil humic acid. *Soil Science* **132**, 200-203.
- Matsuda K. and Schnitzer M. (1971) Reaction between fulvic acid, a soil humic material, and dialkyl phthalates. *Bulletin of Environmental Contamination and Toxicology* **6**, 200-204.
- Meneghel R., Petit-Sarlotte C. and Bloch J. M. (1972) Sur la caractérisation et l'isolement des produits de dégradation d'un acide humique après oxydation peroxyacétique. *Bulletin de la Société Chimique de France* **7**, 2997-3001.
- Neyroud J. A. and Schnitzer M. (1975) The alkaline hydrolysis of humic substances. *Geoderma* **13**, 171-188.
- Rashid M. A. and King L. H. (1970) Major oxygen-containing functional groups present in humic and fulvic acid fractions isolated from contrasting marine environments. *Geochimica et Cosmochimica Acta* **34**, 193-201.
- Schnitzer M. (1977) Recent findings on the characterization of humic substances extracted from soils from widely differing climatic zones. In *Soil Organic Matter Studies*, Vol. II, pp. 117-132. IAEA, Vienna.
- Schnitzer M. and Khan S. U. (1972) *Humic Substances in the Environment*. Dekker, New York.
- Schnitzer M. and Ortiz de Serrá M. I. (1973) The chemical degradation of a humic acid. *Canadian Journal of Chemistry* **51**, 1554-1566.
- Schnitzer M. and Skinner S. I. M. (1974) The peracetic acid oxidation of humic substances. *Soil Science* **118**, 322-331.
- Sharp J. H. (1973) Total organic carbon in seawater. Comparison of measurements using persulfate oxidation and high temperature combustion. *Marine Chemistry* **1**, 211-229.
- Wershaw R. L., Pinckney D. J. and Booker S. E. (1977) Chemical structure of humic acids. I. A generalized structural model. *Journal of Research of the United States Geological Survey* **5**, 565-569.