

THE PERSULFATE OXIDATION OF A SOIL HUMIC ACID

F. MARTIN, C. SAIZ-JIMENEZ, AND F. J. GONZALEZ-VILA

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

Received for publication 5 August 1980; revised 6 November 1980

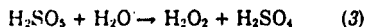
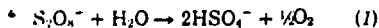
ABSTRACT

We extracted humic acid (HA) from an Encinillas soil, Xeroubrepts, Inceptisols, and oxidized it with potassium persulfate for 2 hours at 140°C. The oxidation products, after methylation, were analyzed by direct injection into a gas chromatographic-mass spectrometric computer system. The most abundant compounds isolated from the HA oxidation products were *n*-C₁₄ and *n*-C₁₆ fatty acids, followed by several benzenecarboxylic and phenolic acids. Dicarboxylic acids and dialkyl phthalates constituted only a relatively small proportion of the isolated compounds. No *n*-alkanes were detected. Persulfate degrades only 40 percent of total weight HA, leaving a residue that can easily be recovered for further structural investigations. Persulfate, therefore, may be used as first oxidant in a sequential HA degradation.

Humic substances are complex polymeric materials that are widely distributed in soils, waters, and sediments. Because of the chemical complexity of humic materials, and in order to get information on the structure, researchers have used several oxidative methods, hoping that the simpler compounds produced would be related to those of the original materials. The main oxidative agents that have been used are potassium permanganate, cupric oxide, and peracetic acid (Schnitzer 1978). With the exception of peracetic acid, the other agents are usually employed under alkaline conditions, which are often drastic and could lead to serious alterations in the chemical structure of the original humic acid (HA) and to the formation of unwanted by-products. However, peracetic acid oxidation of HA afforded a smaller amount of phenolic compounds and a higher amount of benzenecarboxylic acids than did alkaline permanganate oxidation (Schnitzer and Skinner 1974), which suggests that peracetic acid might be as oxidant as permanganate. This feeling is supported by the almost complete degradation of HA—only 25 mg from 1 g of the original HA could be recovered as insoluble residue after peracetic acid oxidation (Schnitzer and Skinner 1974). Thus, the use of mild oxidants that would most likely minimize the extent of undesirable chemical modifications seems worthy of investigation.

Numerous papers have appeared concerning the properties and reactions of persulfuric and

persulfates as oxidant agents. According to Kolthoff and Müller (1951) the decomposition of persulfate in aqueous solutions involves the reactions



In alkaline, neutral, and dilute acid solutions, persulfate decomposes according to reaction (1), though in strongly acid solutions reactions (2) and (3) occur. Evidence is given that potassium persulfate decomposes thermally in aqueous solutions by two reactions (1) a symmetrical rupture of the O—O bond to form two sulfate free-radicals that disappear by reaction with water to liberate oxygen, and (2) an acid-catalyzed reaction involving the unsymmetrical rupture of the O—O bond of the HS_2O_8^- ion to form sulfur tetroxide and bisulfate. In dilute acid solutions, sulfur tetroxide decomposes rapidly to form oxygen and sulfuric acid, but in solutions 2 to 5 *M* in perchloric or sulfuric acid, sulfur tetroxide hydrolyzes rapidly to Caro's acid (H_2SO_5). The activation energy of the uncatalyzed reaction is 33.5 kcal, and for the acid-catalyzed reaction 26.0 kcal.

Recently, Baumgartner (1973) reviewed the use of persulfate as oxidant for alcohols, acids, amides, aldehydes, ketones, and phenols. The reaction rate of phenols with persulfate is related

to the structure and pK of phenols and to the pH and type of solvent. In this oxidation, coupling of phenols was observed.

Furthermore, persulfate oxidation has also been used by Menzel and Vaccaro (1964) for the rapid determination of dissolved organic carbon in seawater in concentrations between 0.1 and 20 mg/liter. The analytical approaches used involve oxidation of organic matter to carbon dioxide, followed by quantitative determination of this product. More recently, Sharp (1973) and Gershey et al. (1979) have shown that the persulfate, as compared with other methods, gives incomplete oxidation of organic carbon to carbon dioxide.

In the search for mild oxidants, we thought it would be worthwhile to study the possible usefulness of persulfate for HA oxidation. We report here an original method that permits the use of potassium persulfate as oxidant reagent for HA structural studies under acid conditions.

MATERIALS AND METHODS

The HA originated from the A1 horizon (10 to 25 cm) of an Encinillas soil, Xeroubrepts, Inceptisols, located at the Coto de Doñana Biological Reservation, southwest Spain. Methods of extraction, purification, and drying of HA were the same as those described previously (Martin et al. 1977). The ultimate and functional group analyses of the purified HA were as follows: 57.1% C, 4.5% H, 3.4% N, 35.0% O, 6.0 meq total acidity, 3.3 meq CO₂H, 2.7 meq phenolic OH, and 0.3 meq OCH₃ per gram.

Different analytical conditions, such as temperature (from 80 to 150°C), reaction time (from 30 min to 4 h), pH of solution (from 2 to 6), oxidant (from 1% to saturation), and sample amount (from 100 to 500 mg), were tested. Those reported herein were the best experimental conditions obtained.

Two hundred milligrams of HA was mixed with 50 ml of saturated potassium persulfate solution and heated for 2 h at 140°C in a digestion bomb Autoclave-3 (Perkin-Elmer) under stirring. The digest was cooled, and an aliquot was analyzed for total amino acids and sugars, yielding 3.0 and 0.7%, respectively. The remainder was transferred to a liquid-liquid extractor and extracted with ethyl acetate for 24 h. The extract was methylated with diazomethane. The methylated oxidation products were analyzed by direct injection into a gas chromatographic-mass spectrometric computer system (Hewlett-Pack-

ard, model 5992 B). The gas chromatographic conditions were 3000 × 3 mm stainless steel column packed with 3% OV-17 on Chromosorb W HMDS 80-100 mesh, programmed from 150 to 270°C at a rate of 4°C per min and then isothermal for 15 min. Helium at a flow rate of 20 ml/min was used as carrier gas. Mass spectrometer conditions were: MS peak detect threshold 50 linear counts, scan speed 690 atomic mass units second, electron multiplier 1400 V, GC peak detect threshold 1000, electron energy 70 eV, and mass range 40 to 800.

The identity of the compounds in each peak was confirmed by running its mass spectrum, searching in the computer library, and matching the mass spectrum with the known compound to which it corresponded, and by cochromatography of known and unknown compounds. No quantitative data are reported because accuracy cannot be ensured by the methods employed, as discussed by Maximov et al. (1977).

The insoluble residue obtained after reaction was 144 mg, and after being washed and dried, it was subjected to digestion twice more. The residues were 127 and 120 mg, respectively. The elementary analysis of the residue was 62.6% C, 4.0% H, 2.5% N, and 30.9% O.

RESULTS AND DISCUSSION

The material removed constituted, in addition to amino acids and carbohydrates (not studied here), oxidation products, also, which are listed in Table 1. Because the oxidation products were methylated prior to the gas chromatographic separations, and in view of the low OCH₃ content of the original HA, it is likely that most of the CO₂H and OH occurred in the initial materials as carboxyls and phenolic hydroxyls, rather than as esters and ethers. Therefore, it may be more realistic to refer to the compounds isolated as phenolic and benzenecarboxylic acids, rather than as esters and ethers (Schnitzer and Skinner 1974).

The most abundant compounds isolated from the HA oxidation products were *n*-C₁₆ and *n*-C₁₈ fatty acids. Major aromatic compounds were benzenepentacarboxylic, 1,2,3,4-benzenetetracarboxylic, and 1,2,4,5-benzenetetracarboxylic acids, followed by 3-hydroxy-1,2,4-benzenetricarboxylic, 2-hydroxy-1,3,5-benzenetricarboxylic, and 3,4-dihydroxybenzoic acids. Dicarboxylic acids and dialkyl phthalates constituted only a relatively small proportion of the compounds isolated and identified. No *n*-alkanes were de-

TABLE 1
Products from the persulfate oxidation of HA

Compounds identified	Oxidations		
	1	2	3
Dimethyl succinate	+		
3-Methoxybenzoic acid methyl ester	+	+	
Dimethyl glutarate	+		
1,2-Benzenedicarboxylic acid dimethyl ester	+		
Diethyl phthalate		+	
<i>n</i> -C ₁₁ fatty acid methyl ester	+		
3,4-Dimethoxybenzoic acid methyl ester	+	+	
<i>n</i> -C ₁₆ fatty acid methyl ester	+	+	+
3-Methoxy-1,2-benzenedicarboxylic acid dimethyl ester	+		
2-Methoxy-1,5-benzenedicarboxylic acid dimethyl ester		+	
1,2,3-Benzenetricarboxylic acid trimethyl ester	+	+	
<i>n</i> -C ₁₆ fatty acid methyl ester	+	+	+
Dibutyl phthalate	+		
1,3,5-Benzenetricarboxylic acid trimethyl ester		+	
3-Methoxy-1,2,4-benzenetricarboxylic acid trimethyl ester	+	+	
2-Methoxy-1,3,5-benzenetricarboxylic acid trimethyl ester	+	+	
1,2,3,4-Benzenetetracarboxylic acid tetramethyl ester	+	+	
1,2,4,5-Benzenetetracarboxylic acid tetramethyl ester	+	+	
1,2,3,5-Benzenetetracarboxylic acid tetramethyl ester	+	+	
5-Methoxy-1,2,3,4-benzenetetracarboxylic acid tetramethyl ester	+	+	
2-Methoxy-1,3,4,5-benzenetetracarboxylic acid tetramethyl ester	+		
Di-(2-ethylhexyl) phthalate	+	+	+
Benzenepentacarboxylic acid pentamethyl ester	+	+	
Methoxy-benzenepentacarboxylic acid pentamethyl ester	+	+	

tected. Methylation of HA prior to oxidation failed to increase the variety and yield of the oxidation products.

According to oceanographers' experience, persulfate give almost complete oxidation of dissolved organic carbon, but not particulate carbon, in seawater (Sharp 1973). This observation suggests that persulfate may attack the most accessible or relatively easily degradable portion of HA.

Schnitzer and Neyroud (1975) have shown

that alkanes and fatty acids could be released from HA by milder treatments involving ultrasonics, water heating at 170°C for 3 h, or both. These treatments released loosely held or physically absorbed aliphatic compounds. Furthermore, it was shown that HA can retain or fix significant amounts of hydrophobic organic compounds, including dialkyl phthalates (Khan and Schnitzer 1972). In addition to fatty acids and dialkyl phthalates, phenolic and benzenedicarboxylic acids were released by persulfate oxidation, indicating that aromatic structures also constitute the easily degradable portion of this HA. Neyroud and Schnitzer (1977) reported that oxidative methods of increasing strength (NaOH, CuO/NaOH, peracetic acid, and KMnO₄) degrade the HA into fractions, but each extracted fraction contains the same basic compounds. The differences among fractions are due to the distinct stability related to the extent of van der Waals forces, hydrogen bonds, and C—O and C—C bonds.

It is noteworthy that most of the phenolic acids identified were also isolated from alkaline permanganate oxidation of lignins and HA cupric oxide oxidation (Griffith and Schnitzer 1976). This indicates that lignin or condensed lignin structures may also be present.

Reaction of persulfate with HA is obviously very complex, and detailed oxidation mechanisms cannot be provided. We suggest that oxidation proceeds through the oxygen atom originated in reaction (1). In this case, the attack of persulfate, as for peracetic acid or permanganate oxidation, may be electrophilic (Schnitzer and Skinner 1974). Coupling products, as reported by Baumgartner (1973), for oxidation of single phenolic compounds were not observed in the analytical conditions used.

To furnish further information about the degradative action of persulfate, it may be interesting to compare the types of products resulting from HA oxidation in acid medium, with the exclusion of nitric acid oxidation, which yields nitrocompounds (Hansen and Schnitzer 1967). Major products resulting from the peracetic acid oxidation of a podzol HA were aliphatic, phenolic, and benzenedicarboxylic acids (Schnitzer and Skinner 1974). Menenghel et al. (1972), using less drastic experimental conditions for peracetic acid oxidation, isolated and identified amino acids and sugars, but failed to detect any phenolic or aromatic compounds among the re-

action products of a peat HA. According to Schnitzer and Skinner (1974), these different results may be attributed to the distinct nature of the HAs used, because the peat HA was less aromatic than are HAs isolated from inorganic soils and is thus not a typical soil HA.

All the compounds reported for peracetic acid oxidation were obtained with persulfate oxidation. Therefore, it appears that both oxidative methods in acid medium afford the same type of reaction products. The main difference between persulfate and peracetic acid oxidation is the extent of the degradation. Peracetic acid degrades about 97.5% of HA and persulfate degrades only 40%, leaving a residue that can easily be recovered. The most resistant moiety of HA or residue could be either the aromatic core or a product of condensation originated during the reaction. Further studies on the nature of this residue, using alkaline oxidations, are in progress. In this connection, Schnitzer and Ortiz de Serra (1973) proposed the study of HA degradation of oxidative methods of increasing strength, because it has been shown that HA contain a relatively easily degradable portion, also shown herein, that might be accessible to mild oxidants. Persulfate, therefore, may be used as first oxidant in a sequential degradation.

ACKNOWLEDGMENTS

We thank T. Verdejo for technical assistance.

REFERENCES

- Baumgartner, J. 1973. Beitrag zur Oxidation pflanzlicher Phenole insbesondere der Ferulonsäure. Thesis E. T. H. Zurich Nr. 4923, Juris-Verlag, Zürich.
- Garshey, R. M., M. D. Mackinnon, P. J. le B. Williams, and R. M. Moore. 1979. Comparison of three oxidation methods used for the analysis of the dissolved organic carbon in seawater. *Mar. Chem.* 7:289-306.
- Griffith, S. M., and M. Schnitzer. 1976. The alkaline cupric oxide oxidation of humic and fulvic acids extracted from tropical volcanic soils. *Soil Sci.* 122:191-201.
- Hansen, E. H., and M. Schnitzer. 1967. Nitric acid oxidation of Danish illuvial organic matter. *Soil Sci. Soc. Am. Proc.* 31:79-85.
- Khan, S. U., and M. Schnitzer. 1972. The retention of hydrophobic organic compounds by humic acid. *Geochim. Cosmochim. Acta* 36:745-754.
- Kolthoff, I. M., and I. K. Müller. 1951. The chemistry of persulfate: I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. *J. Am. Chem. Soc.* 73:3055-3059.
- Martin, F., C. Saiz-Jimenez, and A. Cert. 1977. Pyrolysis gas chromatography mass spectrometry of soil humic fractions: I. The low boiling point compounds. *Soil Sci. Soc. Am. J.* 41:1114-1118.
- Maximov, O. B., T. V. Shveta, and Yu. N. Elkin. 1977. On permanganate oxidation of humic acids. *Geoderma* 19:63-78.
- Menenghel, R., C. Petit-Sarlotte, and J. M. Bloch. 1972. Sur la caractérisation et l'isolement des produits de dégradation d'un acide humique après oxydation peracétique. *Bull. Soc. Chim. France* 7: 2997-3001.
- Menzel, D. W., and R. F. Vaccaro. 1964. The measurement of dissolved organic and particulate carbon in seawater. *Limnol. Oceanogr.* 9:138-142.
- Neyroud, J.-A., and M. Schnitzer. 1977. Structure chimique des acides humiques et fulviques du sol. *In Soil organic matter studies*, vol. 2. IAEA, Vienna, pp. 157-169.
- Schnitzer, M. 1978. Humic substances: Chemistry and reactions. *In Soil organic matter*, M. Schnitzer and S. U. Khan (eds.). Elsevier, Amsterdam, pp. 1-64.
- Schnitzer, M., and J. A. Neyroud. 1975. Alkanes and fatty acids in humic substances. *Fuel* 54:17-19.
- Schnitzer, M., and M. I. Ortiz de Serra. 1973. The chemical degradation of a humic acid. *Can. J. Chem.* 51:1554-1566.
- Schnitzer, M., and S. I. M. Skinner. 1974. The peracetic acid oxidation of humic substances. *Soil Sci.* 118:322-331.
- Sharp, J. H. 1973. Total organic carbon in seawater. Comparison of measurements using persulfate oxidation and high temperature combustion. *Mar. Chem.* 1:211-229.