

DIBORANE REDUCTION OF HUMIC SUBSTANCES

F. Martin¹, F.J. Gonzalez-Vila¹, and G. Almendros²

¹Centro de Edafologia y Biologia Aplicada del Cuarto (C.S.I.C.).
P.O. Box. 1052. 41080-Sevilla. Spain.

²Instituto de Edafologia y Biologia Vegetal (C.S.I.C.).
Serrano 115 dpdo. 28006-Madrid. Spain.

SUMMARY

Changes in the composition and properties of humic substances following repeated treatments with diborane in tetrahydrofuran have been investigated.

Solubility, ionic mobility, elementary composition and spectral characteristics of diborane-treated samples suggest that both humic and fulvic acids undergo a drastic chemical change upon reduction.

The disappearance of the band at 1720 cm^{-1} and the prominent absorption centred at 1010 cm^{-1} in the IR spectra of the reduced samples are noticeable, and may be explained in terms of an efficient transformation of carboxyl groups into alcoholic OH.

These modifications in the distribution of oxygen-containing functional groups, are probably responsible for the reported changes in the colloidal properties and the structural characteristics of the diborane-reduced humic samples.

INTRODUCTION

The complex structure of humic substances (HS) has been investigated by researchers from different scientific disciplines. In recent years, many physical and chemical features have been studied applying sophisticated instrumental techniques, which have made it possible to obtain more information about their characteristics.

Chemical modifications and derivatizations are common in humus chemistry in order to obtain information on the structure of the complex molecules. Thus, humic substances have been methylated, permethylated, acetylated, silanized, fluorinated, etc., for the determination of oxygenated functional groups or for obtaining derivatives useful for spectroscopic and/or chromatographic studies (refs. 1-2).

Other modifications have been reductions using different reagents such as sodium borohydride (reduction of aliphatic carbonyls), Zn-dust distillation (reduction of carboxyl groups in strongly acidic conditions when performed with simultaneous acetylation with acetic anhydride), SnCl_2 in 0.1N NaOH,

(to reduce quinones), etc. (refs. 3-5).

Diborane has been used to determine both active hydrogen and to reduce carbonyl groups in humic substances (refs. 6-7), but further studies of the reduced molecule was not continued due to the difficulties in obtaining diborane. In recent years diborane as well as different diborane complexes have become commercially available, and research on organoboranes has received increasing attention.

In the present study we report the results obtained after treatment of humic and fulvic acids with diborane in tetrahydrofuran (THF). After the reaction was completed, the reduced samples were recovered and examined by physicochemical methods to monitor the changes in the original substances.

MATERIAL AND METHODS

Two fulvic acids and one humic acid were investigated. One of the fulvic acids (PL-FA) was extracted from a Humic Haplorthod. The processes of extraction and purification has been reported elsewhere (ref. 8). The other fulvic acid (FT-FA) was isolated from lake water over a peatland. The water contained particles of iron oxide adsorbing humic substances and silicates. The suspended particles were dialyzed and shaken with cation exchange resin (H^+ form). The resultant liquid was centrifugated at 20,000 g, concentrated at reduced pressure and liophilized. The humic acid (L-HA) was isolated from a lignite by the usual method (ref. 9). An atypical characteristic of this humic acid was its high solubility in some organic solvents.

The samples were dissolved in a minimum amount of THF, and 5 ml of a 1M solution of diborane in THF were slowly added under N_2 atmosphere at a temperature of 0 °C. After completion of the H_2 evolution, the flasks were stoppered under N_2 and heated to 50 °C.

Every second day a small amount of the supernatant was sampled and checked for diborane activity, adding fresh diborane solution when necessary. After 20 days, the excess of diborane was destroyed by addition of water; the THF excess was then evaporated under reduced pressure, and the boric acid formed was removed by evaporation following the repeated addition of methanol.

Elemental analyses were carried out with a Hewlett-Packard CHN-185 microanalyzer. The FTIR spectra were recorded using KBr pellets in a Nicolet 5DXE spectrophotometer, adding 100 interpherograms at a 2 cm^{-1} resolution. The ^{13}C -NMR spectra were registered with a Bruker MSL 300 spectrophotometer at 75.4 MHz under conditions of broad band decoupling and pulse delays of 0.5 s; 30,000 free induction decays were accumulated for each sample. Cellulose acetate electrophoresis were carried out at 200 V, using a phosphate buffer at pH=7.

RESULTS AND DISCUSSION.

Table 1 shows the elemental analysis of the samples before (HA,FA) and after (RFA, RHA) diborane treatment.

TABLE 1

Sample	Ashfree percentages				Atomic ratios	
	C	H	N	O	H/C	O/C
PL-FA	44.63	2.72	0.20	52.45	0.73	0.88
PL-RFA	54.21	5.26	2.75	37.78	1.16	0.52
FT-FA	38.07	3.14	1.16	57.63	0.99	1.14
FT-RFA	45.90	3.50	1.27	49.33	0.92	0.81
L-HA	53.29	2.94	1.46	42.31	0.66	0.60
L-RHA	56.60	5.91	0.56	36.94	1.25	0.49

The elemental analysis showed the classical changes which occur to single compounds upon reduction, i.e., an increase in the C and H content and a decrease in the oxygen, while the changes in the N content may be related to the nature of this element in each sample. Consequently, the atomic H/C vs O/C ratios, when represented on a Van Krevelen diagram (ref. 10), showed the expected shifts of a reduction process.

The UV and visible spectra were featureless both in the original and reduced samples, but the values for specific extinction of the latter highly diminished through the whole wavelength range, as corresponding to the expected reduction of the chromophore and/or auxochrome functional groups.

Figure 1 shows the FTIR spectra of the original and reduced samples. Striking changes were evident between samples. Diborane reduction resulted in a sharpening in the OH absorption band near 3400 cm^{-1} which suggested a simplification in the band system after the disappearance of most of the hydrogen bonding. Due to the negligible intensity of the band at 1720 cm^{-1} , the OH absorption bands may be more characteristic of phenolic and alcoholic OH groups (ref. 11).

The bands at 2920 and 2860 cm^{-1} generally overlapped in a shoulder of

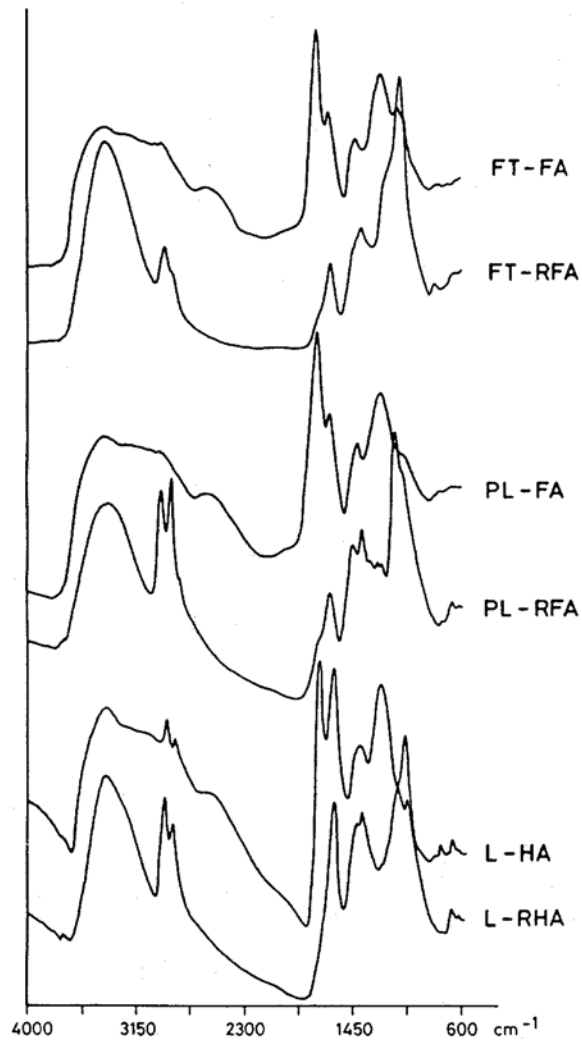


Fig. 1. FTIR spectra of the original and reduced fulvic and humic acids.

the broad O-H stretching band, and its enhanced resolution in the reduced samples may be explained in terms of the reduction in the broadness of the OH band but also by the change of COOH into CH₂OH groups.

The C-O stretching absorption at 1720 cm⁻¹ practically disappeared after diborane treatment of the humic and fulvic acids. The same occurred to the broad carboxyl absorption band near 2600 cm⁻¹ and for the band centred at 1230 cm⁻¹, assigned to the C-O stretching vibration or OH deformation of carboxyl groups (ref. 5).

In the reduced samples a sharp band around 1010 cm⁻¹ appeared; the increased intensity of which agreed with the expected formation of alcoholic OH groups. In the case of FT-FA, the relative intensities of the different absorption bands resembled those of neutral polysaccharides, and in the other two samples, where the aliphatic bands at 2920 and 1450 cm⁻¹ became prominent, the IR spectra suggested a polymeric structure consisting of aliphatic and/or cyclic structural components supporting low-polarity oxygen containing functional groups.

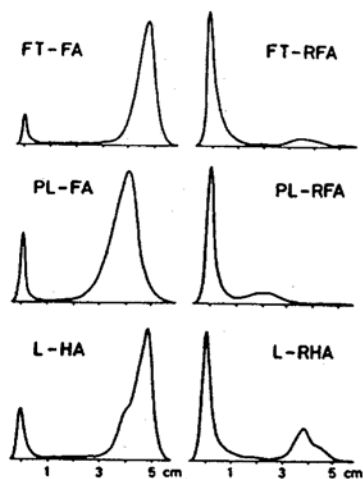


Fig. 2. Cellulose acetate electrophoresis of original and reduced humic substances

Figure 2 shows the electrophoregrams of the studied samples, illustrating their different behaviour following the suggested reaction, i.e., the lower ionic mobility of the reduced samples, which may be explained on the basis of their lower polarity due to the practical absence of carboxyl groups.

High resolution ¹³C-NMR spectra of the original samples are shown in Fig. 3. After diborane treatment, all the samples gave NMR spectra similar to that shown for L-RHA (Fig 3, bottom).

The spectra of the original samples were poorly resolved and showed only broad absorption bands, as may be expected for complex molecular systems in which intermolecular H-bridges has probably a significant influence on the structural complexity. Similar NMR spectra have been presented for humic acids by several authors (refs.12-14).

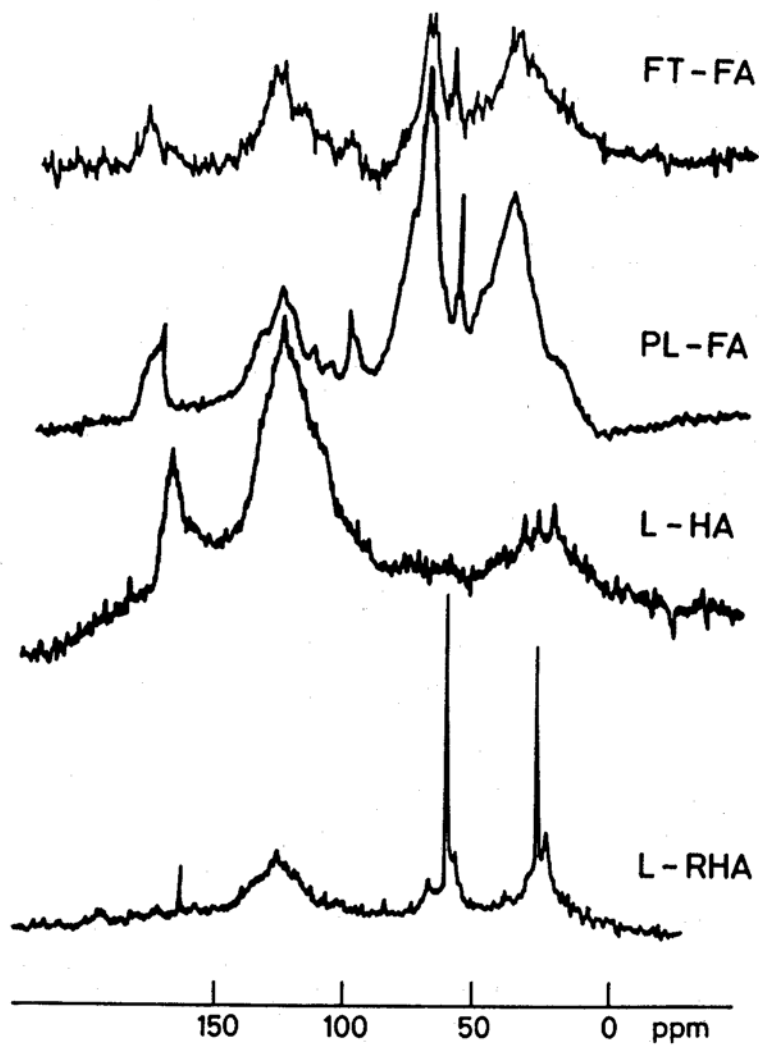
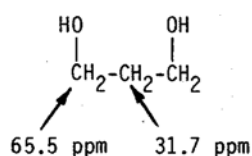


Fig. 3. Changes in the ^{13}C -NMR patterns of the three studied samples (above) after diborane treatment (below).

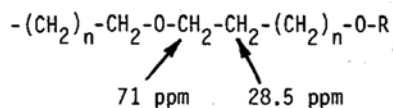
The convergence in the ^{13}C -NMR pattern of the samples after reduction indicates the formation of similar structures from samples of a very different initial nature.

Changes observed after reduction corresponded to the disappearance of the resonances for carboxyl C atoms at about 173-176 ppm, a high decrease of the broad absorption envelope in the 110-160 ppm region, assigned to the various sp^2 C atoms from aromatic rings or olefins and, in the case of the FA samples, the absence of the bands in the 55-110 ppm range, assigned to resonances of O and N-substituted carbons.

In the original samples signals of a random mixture of paraffinic carbons appeared in the 0-50 ppm region. This drastically changed to two sharp signals at 28 and 62 ppm. According to the literature (ref. 15) these peaks can be assigned either to 1,4 butanediol structures:



or to a polymer of the following type:



Since the samples were dried overnight in a high-vacuum system to eliminate possible THF residues (dominant shifts at 68.4 and 26.5 ppm), the above-mentioned changes seem to be characteristic of the diborane treatment.

In conclusion, it has been confirmed that diborane treatment may be a useful method for obtaining chemically transformed humic substances. The striking changes in the distribution of the functional groups will produce not only changes in their solubility and colloidal properties, but also in the nature of the different intramolecular forces affecting the structural arrangement of the polymer constituents. Further studies applying adequate methods for the specific properties of the reduced preparations will be necessary to obtain information on the nature of the diborane-transformed humic substances, which subsequently could be related to the chemical structure of the untreated samples.

Acknowledgement .- We wish to thank Dr. R. Fründ of Regensburg University (West Germany) for the ^{13}C -NMR measurements.

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