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^{31}P NMR Spectroscopy in Wood Chemistry

Part IV. Lignin Models: Spin Lattice Relaxation Times and Solvent Effects in ^{31}P NMR

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Summary

A variety of lignin-like model compounds were derivatized with 1, 3, 2-dioxaphospholanyl chloride (I). Their phosphorus spin lattice relaxation times (T_1) were of the order of 5 s for phosphorus nuclei attached to carboxylic acids while the relaxation times of phenol and alcohol derivatives were around 9 and 8 s respectively.

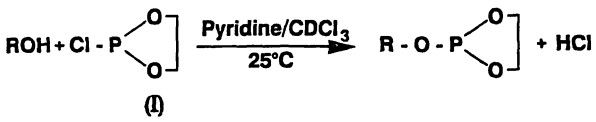
The ^{31}P chemical shifts of the derivatives of monofunctional alcohols moved downfield when the samples were diluted with $CDCl_3$ and upfield when diluted with pyridine. The concentration dependency of the ^{31}P chemical shifts of the phenol derivatives was considerably less than that of the alcohol derivatives. The carboxylic acid derivatives showed almost no concentration dependence. The ^{31}P chemical shifts most sensitive to solvent concentration were the primary hydroxyls in β–O–4 model compounds of lignin. *Alpha* and guaiacyl hydroxyls were only slightly sensitive to solvent concentration.

The resolution of the ^{31}P NMR spectra of lignins can be significantly improved by exploiting these solvent effects. Signals due to primary and secondary alcohols present in lignin may be readily resolved by appropriately adjusting the solvent concentration during spectral acquisition.

The presence of the ionic salt, pyridine hydrochloride, appears to be responsible for the observed concentration dependence of the chemical shifts.

Introduction

Parts I and II of this series of papers reported on the reaction of 1,3,2-dioxaphospholanyl chloride (I) with monosaccharides, polysaccharides, lignin-carbohydrate complexes, and a wide variety of model compounds for lignin (Archipov *et al.* 1991, Parts I and II). In this reaction (Scheme 1), the labile protons in lignins were easily derivatized with trivalent phosphorus nuclei, which can then be subject to ^{31}P NMR analysis. ^{31}P, with its non-zero spin (I = 1/2), is the only naturally occurring isotope of phosphorus. Therefore, it is an ideal nucleus for determining the chemical structure of phosphorus-containing compounds by means of nuclear magnetic resonance spectroscopy (^{31}P NMR). When this novel technique was applied to soluble lignins, it proved a powerful means of probing their structures.



(I)

Where R = Residues of phenols, alcohols, aldehydes, sugars, carboxylic acids

Scheme 1. The derivatization reaction used throughout this work: the reaction of 1,3,2-dioxaphospholanyl chloride (I) with labile protons.

The principle underlying the method is as follows: In the presence of a magnetic field nuclei such as ^{31}P, ^{13}C, and ^{1}H undergo transitions that raise them to a higher energy state. The high energy nuclei may dissipate energy (relax), in a process termed spin lattice relaxation (T_1), by exchanging energy with externally fluctuating electromagnetic fields. The field may arise from the nearby solvent molecules or an array of neighbouring atoms either in the same molecule or in other molecules. The rate of spin lattice relaxation determines the rate of absorption of electromagnetic energy by the nucleus during an NMR experiment, and may significantly affect the intensities of the NMR signals. The proper choice of flip angle and delay time between successive pulses demands a knowledge of the spin lattice relaxation times of the nuclei.

The phenomenon of concentration dependence of the chemical shifts is well known in proton NMR spectroscopy (Kemp 1978). It is caused mainly by intermolecular hydrogen bonding between a polar solvent and compounds bearing functional groups such as OH, NH, or SH.

The transfer of an electron cloud from the hydrogen to the neighbouring electronegative atom causes the hydrogen atom to experience a deshielding effect. This effect is strongest when the hydrogen bond is