and at 38 and 91 ppm in the ^{13}C spectrum. When the latter spectrum is off-resonance decoupled, each of these two resonances is observed as a triplet. Previous spectral studies have shown that when alkenes or alkynes form adducts with the sulfido ligands in I, the resonance assigned to the methanedithiolate ligand, originally observed at 2.53 ppm, undergoes a large downfield shift.[5] The resonances near 6 (^1H) and 90 ppm (^{13}C) in the spectra of II have chemical shifts similar to those observed for other adducts of I and are therefore assigned to the methylene group of the methanedithiolate ligand.

The synthesis of II by an alternate route provides additional support for its proposed formulation. The reaction of formaldehyde with hydrogen sulfide in the presence of an acid catalyst has been previously reported to yield the transient thioformaldehyde molecule, which rapidly trimerizes to form trithiane.[10] A similar reaction in the presence of I (eq 2) takes advantage of

$$I + H_2CO/H_2O + H_2S \xrightarrow[THF]{25\ ^\circ C} II \qquad (2)$$

the high affinity of the sulfido ligands in the complex for the thioaldehyde and forms complex II in 75% yield. Additional studies of II are described below.

The ability of I to promote the reductions of other cumulenes has been established previously. For example, allenes and ketenes react with I to form stable adducts in which an olefinic bond has interacted with the sulfido ligands to produce new 1,2-dithiolate ligands.[5] Each of the allene or ketene adducts reacts with hydrogen under mild conditions (60 °C, 1–2 atm) to form the free alkene or aldehyde, respectively, and to regenerate I.[5] The presence of excess cumulene inhibits the reactions with hydrogen, and the systems are not catalytic. In contrast, carbon disulfide does not form a stable adduct with I, but under hydrogen pressures it is reduced catalytically. The NMR spectrum of I in carbon disulfide is identical with its spectrum in $CDCl_3$; however, in a tube sealed under hydrogen pressure (1–2 atm) the former spectrum shows significant shifts in the resonances of I.[11] After a period of 2–3 weeks at 70 °C, the spectrum in carbon disulfide shows the presence of an approximately equal molar ratio of I and II, ~5 mol of H_2S/mol of I, and other organosulfur products (vida infra). Even when reaction 1 is carried out under much higher hydrogen pressures (16.5 atm), it does not go to completion after 2–3 weeks at 75 °C; significant amounts (>50%) of I are recovered. Additional experiments, which are discussed below, have confirmed that under hydrogen pressure, II undergoes a further reaction that regenerates I and results in a catalytic cycle.

The interaction of thioformaldehyde with the sulfur bridges in the molybdenum dimer II can be reversed under a variety of mild conditions. Although II is stable in the presence of air and moisture at 25 °C, it reacts with ethylene at this temperature to form the known ethylene adduct $(CH_3C_5H_4Mo)_2(S_2CH_2)(SC_2H_4S)$.[5] In a sealed NMR tube at 75 °C under nitrogen pressure, II dissociates in $CDCl_3$ to form I and trithiane. No other products are detected by NMR. The reaction is very slow under these conditions; after a period of 14 days, the ratio of I:II is approximately 0.4. Under similar conditions II reacts with hydrogen (1–2 atm) in $CDCl_3$ to regenerate I. The organosulfur products that are produced in the latter reaction result in a complex set of resonances in the ^1H NMR spectrum between 3 and 4.2 ppm. Methanethiol, dimethyl disulfide, and hydrogen sulfide, which would be possible products in this reaction, are not detected. In a separate experiment we have established that methanethiol also reacts with II to produce I. Organosulfur products that are characterized by NMR resonances between 3 and 4 ppm are again observed. Further studies will be necessary to completely identify these products. Relatively few reactions of thioaldehydes, either generated in solution[12–14] or stabilized by coordination to one or more metal ions,[15–17] have been characterized. We anticipate that the ability of II to function as a source of free thioformaldehyde or of the unusual sulfur-coordinated species will play a useful role in establishing the reaction chemistry of this molecule. Further studies of the ability of I to mediate the hydrogenolyses of related heterocumulenes and of aromatic organosulfur compounds are in progress.

Acknowledgment. Support from the National Science Foundation, the Department of Energy, Office of Basic Energy Sciences, and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. I, 85565-70-4; II, 85565-71-5; H_2CS, 865-36-1; CS_2, 75-15-0.

(10) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1960; Vol. III, p 150.

(11) The Cp resonance shifts upfield from 6.27 to 5.80 ppm and the S_2CH_2 resonance shifts downfield from 2.68 to 3.54 ppm. Similar shifts have been observed when the sulfido ligands in I undergo adduct formation.[5] A new resonance is observed at 1.83 ppm, which may be associated with an SH functionality, but the NMR data do not permit a structural assignment for the intermediate.

(12) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.

(13) Wilson, S. R.; Georgiadis, G. M., Khatri, H. N.; Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 3577.

(14) Vedejs, E.; Arnost, M. J.; Dolphin, J. M.; Eustache J. *J. Org. Chem.* **1980**, *45*, 2601 and references within.

(15) (a) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73; (b) *J. Chem. Soc., Chem. Commun.* **1977**, 901.

(16) (a) Adams, R. D.; Katahira, D. A. *Organometallics* **1982**, *1*, 460. (b) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *Ibid.* **1982**, *1*, 240.

(17) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

Isotopic Multiplets in the Proton-Decoupled Carbon-13 NMR Spectra of Carbohydrates with Partially Deuterated Hydroxyls

Jacques Reuben

Hercules Incorporated, Research Center
Wilmington, Delaware 19899

Received December 6, 1982

The effect of deuterium substitution on carbon-13 chemical shifts is well-known in the art. Specific deuterium labeling is often used for spectral assignments. Partial deuteration of hydroxyl groups of carbohydrates dissolved in Me_2SO leads to isotope shifts and splitting of the resonances of the carbon atoms bearing such groups.[1] In alcohols and phenols in Me_2SO solutions, the resonances of carbon atoms vicinal to hydroxylated carbons are also shifted, but to a lesser extent.[2] Individual spectra of protonated and deuterated sugars in Me_2SO have been compared.[3] More extensive measurements of isotope effects on carbon-13 chemical shifts of carbohydrates have been carried out in concentric sample tubes, one containing H_2O and the other D_2O solutions.[3,4] Analysis of the data resulted in separation of the β-effect (due to deuteration of a directly bonded hydroxyl), in the range 0.11–0.15 ppm, and the γ-effect (due to deuteration of a hydroxyl on a vicinal carbon), in the range 0.03–0.06 ppm.[4] The hydrogen-exchange rate of hydroxyl groups in Me_2SO solutions is usually sufficienty slow to allow the direct observation of shifts of such magnitude.[2] Direct observation of new peaks slightly displaced from those observed for the protio forms in the spectra of carbohydrates with partially deuterated hydroxyls should permit the assignment of the affected carbons with respect to hydroxyls on vicinal carbons as well as relative to directly bonded hydroxyls.

This communication presents a demonstration of multiplet structures in the proton-decoupled carbon-13 NMR spectra of

(1) Gagnaire, D.; Vincendon, M. *J. Chem. Soc., Chem. Commun.* **1977**, 509–510.

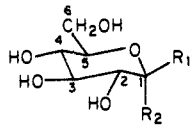
(2) Newmark, R. A.; Hill, J. R. *Org. Magn. Reson.* **1980**, *13*, 40–44.

(3) Ho, S. C.; Koch, H. J.; Stuart, R. S. *Carbohydr. Res.* **1978**, *64*, 251–256.

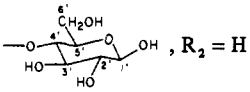
(4) Pfeffer, P. E.; Valentine, K. M.; Parrish, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 1265–1274.

0002-7863/83/1505-3711$01.50/0

Chart I

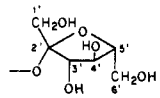


1, $R_1 = H; R_2 = OH$



4, $R_1 =$, $R_2 = H$

2, $R_1 = OH; R_2 = H$



5, $R_1 = H, R_2 =$

3, $R_1 = H; R_2 = OCH_3$

Table I. Classification of Carbon Atoms According to Expected Isotope Effects

type	species	isotopic shift	rel abundance
β	1, COH	0	R
	2, COD	Δ_β	1
$\beta\gamma$	1, HOCCOH	0	R^2
	2, HOCCOD	Δ_γ	R
	3, DOCCOH	Δ_β	R
	4, DOCCOD	$\Delta_\beta + \Delta_\gamma$	1
$\beta\gamma\gamma'$	1, HOCC(OH)COH	0	R^3
	2, HOCC(OH)COD	Δ_γ	R^2
	3, DOCC(OH)COH	$\Delta_{\gamma'}$	R^2
	4, DOCC(OH)COD	$\Delta_\gamma + \Delta_{\gamma'}$	R
	5, HOCC(OD)COH	Δ_β	R^2
	6, HOCC(OD)COD	$\Delta_\beta + \Delta_\gamma$	R
	7, DOCC(OD)COH	$\Delta_\beta + \Delta_{\gamma'}$	R
	8, DOCC(OD)COD	$\Delta_\beta + \Delta_\gamma + \Delta_{\gamma'}$	1
γ	1, CCOH	0	R
	2, CCOD	Δ_γ	1
$\gamma\gamma'$	1, HOCCCOH	0	R^2
	2, HOCCCOD	Δ_γ	R
	3, DOCCCOH	$\Delta_{\gamma'}$	R
	4, DOCCCOD	$\Delta_\gamma + \Delta_{\gamma'}$	1

carbohydrates with partially deuterated hydroxyls. The monosaccharides α-D-glucopyranose (**1**, Chart I), β-D-glucopyranose (**2**), and methyl α-D-glucopyranose (**3**) and the disaccharides β-cellobiose (**4**), β-D-glucopyranosyl(1→4)-β-D-glucopyranose, and sucrose (**5**), α-D-glucopyranosyl(1→2)-β-D-fructofuranose, were studied.

Experimental Section. Carbohydrates were obtained from commercial sources. They were dissolved in H_2O/D_2O mixtures and freeze-dried. Solutions of ca. 5% w/v in Me_2SO-d_6 were prepared, treated with $CaSO_4$ (nonindicating Drierite) to remove residual water, and filtered before the recording of spectra. Alternatively, a calculated amount of D_2O can be added to a 5% w/v solution of the carbohydrate in Me_2SO-d_6, followed by $CaSO_4$ treatment and filtering.[2] Carbon-13 NMR spectra were recorded at 90.79 MHz at 27 ± 1 °C on a Nicolet 360 WB NMR spectrometer operating in the pulsed Fourier transform mode. In order to reduce sample heating, broad-band proton decoupling was applied only during data acquisition. The central peak of the solvent resonance was used as an internal reference with a chemical shift of 41.1 ppm relative to TSP. The proton/deuteron mole ratio, R, was determined from the relative intensities of the corresponding spectral components in the resonance of C6 of each of the carbohydrates.

Results and Discussion. The carbon atoms in carbohydrates can be classified into five general types according to their hydroxyl group environment and expected β- and γ-isotope effects. This classification along with the enumeration of the partially deuterated species is summarized in Table I. Assuming statistical distribution, the probability of occurrence of each species is a function of the mole fractions of hydrogen, f_H, and deuterium, f_D ($R = f_H/f_D$). Listed in the last column of Table I are the expected relative intensities of the spectral lines due to each species, taking the fully deuterated species as unity. In the context of the present discussion, the isotopic state of a hydroxyl group ("light" or "heavy") is analogous to the spin state of a spin $^1/_2$ nucleus ($+^1/_2$ or $-^1/_2$) in a magnetic field. The resonances of carbon atoms in the vicinity of partially deuterated hydroxyl groups exhibit multiplicities in accord with this analogy, i.e., the isotopic multiplets are similar to those due to spin–spin couplings. Examples of the spectral types observed in this work are given in Figure 1.

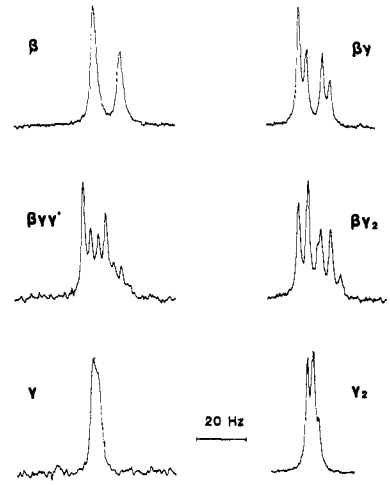


Figure 1. Multiplets in the proton-decoupled carbon-13 NMR spectra of carbohydrates with partially deuterated hydroxyls (see Table I). β, C-6 of methyl α-D-glucopyranose (**3**; $R = 1.6$); $\beta\gamma$, C-2 of **3**; $\beta\gamma\gamma'$, C-2 of β-D-glucopyranose (**2**; $R = 1.9$); $\beta\gamma_2$, C-3 of **3**; γ, C-1 of β-cellobiose (**4**; $R = 1.3$); γ_2, C-5 of **3**. Note the overlap of lines 4 and 5 in the $\beta\gamma\gamma'$ spectrum (see Table I), which is due to the accidental equality $\Delta_\gamma + \Delta_{\gamma'} = \Delta_\beta$.

Type β. A carbon atom of this type bears a hydroxyl group, while none of the vicinal carbons is hydroxylated. When the hydroxyl is partially deuterated, the resonance of such a carbon atom is a doublet with a spacing of Δ_β. The C6 of a hexopyranose is of this type.

Type γ. A nonhydroxylated carbon atom with one hydroxylated neighbor is of type γ. When the hydroxyl is partially deuterated, the carbon-13 resonance of such an atom is a doublet with a spacing of Δ_γ. The C1 of a methyl hexopyranoside is of this type.

Type $\beta\gamma$. A hydroxylated carbon atom with one hydroxylated neighbor is of this type. When the hydroxyls are partially deuterated, the ^{13}C resonance of such a carbon atom is a doublet of doublets with spacings Δ_β and Δ_γ.

Type $\beta\gamma\gamma'$. A hydroxylated carbon atom with two hydroxylated neighbors is of type $\beta\gamma\gamma'$. The isotopic multiplet is now a double doublet of doublets with spacings Δ_β, Δ_γ, and $\Delta_{\gamma'}$. The degenerate type $\beta\gamma_2$ occurs when $\Delta_\gamma = \Delta_{\gamma'}$. The isotopic multiplet is now a doublet of triplets with relative intensities (from low to high field) of R^3:$2R^2$:R:R^2:$2R$:1.

Type $\gamma\gamma'$. If the carbon atom itself is not hydroxylated, but both of its neighbors are, it is of type $\gamma\gamma'$. The expected isotopic multiplet for this type is a doublet of doublets. The degenerate type γ_2 occurs when $\Delta_\gamma = \Delta_{\gamma'}$. The multiplet is now a triplet with relative intensities (from low to high field) of R^2:$2R$:1. Carbon-2 of the fructose moiety of sucrose, which was expected to be a quartet of type $\gamma\gamma'$, appeared as a sharp doublet with $\Delta_\gamma = 0.017$ ppm and, apparently, $\Delta_{\gamma'} = 0$.

The spectral type of each carbon atom in the five carbohydrates is listed in Table II. Unequivocal assignments are possible for most of the spectral bands just from examination of the patterns. An interesting example (shown in Figure 2) is the spectral region containing the resonances of carbons 2′, 3′, and 5′ of β-cellobiose (**4**). The primary assignment of this region to the particular carbon atoms is based on well-known substituent effects. However, the detailed assignment of each peak to an individual carbon atom has been subject to considerable controversy in the literature.[4,5]

(5) Gast, J. C.; Atalla, R. H.; McKelvey, R. D. *Carbohydr. Res.* **1980**, *89*, 137–146 and references therein.

Table II. Deuterium Isotope Effects[a] on Carbon-13 Chemical Shifts of Carbohydrates

		C1	C2	C3	C4	C5	C6
α-D-glucopyranose (1)		βγ	$\beta\gamma_2$	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β	97	108	99	104		117
	Δ_γ	b	39	43	36	23	
β-D-glucopyranose (2)		βγ	βγγ′	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β	104	101	100	100		117
	Δ_γ	17	34; 67	45	31	23	
methyl α-D-glucopyranoside (3)		γ	βγ	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β		107	102	104		117
	Δ_γ	17	35	44	36	25	
β-cellobiose (4)							
β-D-glucopyranosyl		γ	βγ	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β		105	94	93		112
	Δ_γ	17	28	44	31	24	
β-D-glucopyranose		βγ	βγγ′	βγ	γ	γ	β
	Δ_β	101	105	100			110
	Δ_γ	10	39; 66	41	20[b]	17[b]	
sucrose (5)							
α-D-glucopyranosyl		γ	βγ	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β		102	100	101		115
	Δ_γ	b	34	40	36	20	
β-D-fructofuranose		β	γγ′	$\beta\gamma_2$	βγ	γ_2	β
	Δ_β	99		101	100[b]		110
	Δ_γ		0, 17[c]	41	45[b]	24	

[a] Upfield shift in ppb ±5. [b] Line(s) broadened. [c] Appears as a doublet.

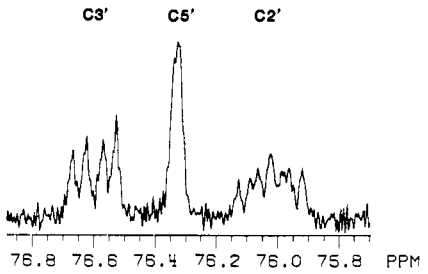


Figure 2. 75.8–76.8 ppm region of the proton-decoupled carbon-13 NMR spectrum of β-cellobiose (**4**) with partially deuterated hydroxyls ($R = 0.86$).

With the present approach the assignment proceeds in a straightforward fashion. The key here is the different spectral type for each carbon atom in the spectrum of the substance with partially deuterated hydroxyls. Thus, C5′ is the only non-hydroxylated one among the three carbon atoms; with one hydroxylated neighbor (C6′), it is of type γ. One of the other two carbons, C2′, has two hydroxylated neighbors (C1′ and C3′) and is of type βγγ′, whereas the second, C3′, has only one hydroxylated neighbor (C2′) and is of type βγ.

A summary of the β- and γ-isotope effects, Δ_β and Δ_γ, measured for the five carbohydrates is also given in Table II. The shifts between the fully protonated and fully deuterated species are in excellent agreement with the results of Ho et al.[3] The observed trends, but not the absolute values, are in agreement with the data of Pfeffer et al.[4] The largest discrepancy is observed for C6 of all species. The directly observed Δ_β(C6) in Me_2SO is in the range of 0.110–0.117 ppm, whereas for aqueous media values of 0.14 and 0.15 ppm have been reported.[4] Thus, a solvent dependence of the isotope effect is indicated.

The present direct measurements provide further details on the structural trends of the isotope effects. In the glucopyranose series one finds the trends $\Delta_\beta(C_6) > \Delta_\beta(C2) > \Delta_\beta(C4) \approx \Delta_\beta(C3)$ and Δ_γ (C2, trans anomeric OH) $> \Delta_\gamma(C3) > \Delta_\gamma(C2) \approx \Delta_\gamma(C4) > \Delta_\gamma(C5) > \Delta_\gamma(C1)$. Such trends should be useful in structure elucidation.

Upon heating of the β-cellobiose sample by continuous decoupling, most of the lines broadened, and for some carbons, the multiplet structure collapsed. The least affected was the multiplet of C3′. Thus, the involvement of the hydroxyl on C3′ as a proton donor in an intramolecular hydrogen bond is indicated. Studies of differential line broadenings induced by temperature or by additives catalyzing hydrogen exchange should permit the determination of relative labilities and acidities of the hydroxyl hydrogens.

Acknowledgment. I am grateful to Herbert T. Conner for his expert assistance and to John C. Gast for helpful discussions and encouragement.

Registry No. 1, 492-62-6; **2**, 492-61-5; **3**, 97-30-3; **4**, 13360-52-6; **5**, 57-50-1; deuterium, 7782-39-0.

A 200% Efficient Electrolysis Cell

Ray Jui-Hsiang Chan, Chihiro Ueda, and Theodore Kuwana*

Department of Chemistry, The Ohio State University Columbus, Ohio 43210

Received January 28, 1983

We report the concept and experimental demonstration of an electrosynthetic scheme is which a common reactant is oxidized to the same product is both the anodic and cathodic compartments of an electrolysis cell. Thus, the prduct yield is potentially twice (200%) the overall efficiency of a conventional cell. The oxidation in the cathodic compartment is accomplished via the electrocatalytic generation of a strong oxidizing agent, hydrogen peroxide, which reacts chemically with a solution species, R, to produce a product, P, which is also produced anodically. The reactions are given is eq 1–3. Essential to this scheme is the identity of product, P, produced in both reactions 1 and 3.

anode $$R = P + ne^- \qquad E_1^{\circ\prime} \qquad (1)$$

cathode $$O_2 + 2e^- + 2H^+ \xrightarrow[cat]{} H_2O_2 \qquad E_{cat}^{\circ\prime} \qquad (2)$$

and $$H_2O_2 + 2H^+ + R \rightarrow P + 2H_2O \qquad (3)$$

When $E_1^{\circ\prime} \leq E_{cat}^{\circ\prime}$, the reverse of reaction 1 may occur at the cathode depending on the electrochemical reversibility of this reaction. For such cases, it may be necessary to use batch reaction or flow-stream removal of H_2O_2 away from the cathode prior to reacting with R.

The selective and quantitative conversion of O_2 to H_2O_2 can be accomplished in the cathodic compartment through the use

0002-7863/83/1505-3713$01.50/0