narrow: we hope that the resultant reversed substituent effect may be an observation of use in other mechanistic investigations of stereoelectronic control.

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Rate Constants for the Reactions of Free Radicals with Oxygen in Solution[1]

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Abstract: The kinetics of the reactions of several free radicals with oxygen have been examined in solution at 300 K using laser flash photolysis techniques. The reactions of resonance-stabilized radicals are only slightly slower than those of nonstabilized radicals: for example, for *tert*-butyl (in cyclohexane), 4.93×10^9; benzyl, 2.36×10^9 (in cyclohexane); cyclohexadienyl (in benzene), 1.64×10^9 M^{-1} s^{-1}. The reaction of *n*-$Bu_3Sn^{\cdot}$ radicals is unusually fast (7.5×10^9 M^{-1} s^{-}), a fact that has been tentatively attributed to a relaxation of spin selection rules due to heavy atom effects.

Liquid-phase autoxidations play an important role in the synthesis of oxygenated organic compounds and in the oxidative degradation of materials as varied as plastics, lubricating oils, and living organisms.[3] Although these processes all involve the reaction of free radicals with atmospheric oxygen, there have been rather few determinations of the rate constants for these reactions. To a large extent, this lack of accurate kinetic data reflects the fact that under most conditions the reaction of free radicals with oxygen is not the rate-determining step in the propagation of the autoxidation chain. That is, of the two propagating steps:

$$R\cdot + O_2 \xrightarrow{k_{Ox}} ROO\cdot \tag{1}$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \tag{2}$$

it is reaction 2 that is generally rate controlling. A great many rate constants have therefore been determined for this reaction.[4,5]

The few published rate constants for reaction 1 for carbon-centered radicals range from as low as 4×10^6 M^{-1} s^{-1} all the way up to 5×10^9 M^{-1} s^{-1} in fluid solution at ambient temperatures.[6-17] While some of the differences in k_{Ox} values may reflect genuine differences in reactivity due to differences in radical structure, in many cases the differences must reflect either experimental error or inaccurate assumptions regarding reactions occurring in competition with radical scavenging by oxygen. The most notable of the "slow" $R\cdot + O_2$ reactions in solution are those for which $R\cdot$ is benzyl or a benzylic type of radical.[6-9] Reported[6-9] rate constants are in the range $2.5–6.8 \times 10^7$ M^{-1} s^{-1} (though a higher value has been found in the gas phase).[18] A slow reaction between O_2 and the benzyl radical might be attributed to the resonance stabilization of this radical. However, other resonance-stabilized radicals of the allylic and pentadienylic type have been reported to react with O_2 more rapidly,[14] while stabilized hydroxyalkyl radicals have k_{Ox} values $\geq 10^9$ M^{-1} s^{-1}.[13,19]

The possibility that the benzyl radical has an anomalously low reactivity toward oxygen has led us to measure the rate constant

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Table I. Kinetic Data for the Scavenging of Various Free Radicals by Oxygen at 300 K

radical	solvent	k_{Ox}, M^{-1} s^{-1} [a]	λ_{ex} [b]	λ_{mon} [b]	O_2 solub.[c]	Table[d]
$PhCH_2\cdot$	hexane	$(2.78 \pm 0.32) \times 10^9$	308	317	0.01477	II
$PhCH_2\cdot$	cyclohexane	$(2.36 \pm 0.22) \times 10^9$	308	317	0.01153	III
$PhCH_2\cdot$	hexadecane	$(1.04 \pm 0.05) \times 10^9$	308	317	0.01725	IV
$PhCH_2\cdot$	benzene	$(2.88 \pm 0.50) \times 10^9$	308	317	0.00919	V
$PhCH_2\cdot$	acetonitrile	$(3.42 \pm 0.17) \times 10^9$	308	317	0.0080	VI
$PhCH_2\cdot$	2-propanol	$(2.51 \pm 0.38) \times 10^9$	308	317	0.01074	VII
$Me_3C\cdot$	cyclohexane	$(4.93 \pm 0.12) \times 10^9$	308	320	0.01153	VIII
c-$C_6H_7\cdot$	benzene	$(1.64 \pm 0.15) \times 10^9$	337	315	0.00919	IX
$(C_2H_5)_2N\dot{C}HCH_3$	benzene	$(4.9 \pm 3.1) \times 10^9$	337	360	0.00919	X
$CH_3\dot{C}(OH)CH_3$	2-propanol	$(3.92 \pm 0.74) \times 10^9$	308	355	0.01074	XI
n-$Bu_3Ge\cdot$	benzene	$(2.50 \pm 0.34) \times 10^9$	308	315	0.00919	XII
n-$Bu_3Sn\cdot$	benzene	$(7.5 \pm 1.4) \times 10^9$	337	380	0.00919	XIII

[a] Errors reported as twice the standard deviation. [b] In nm. [c] Molar concentration of oxygen under 1 atm partial pressure, taken from ref 30. [d] Supplementary table giving full kinetic details.

for this reaction at ambient temperatures with high precision, using the technique of laser flash photolysis. We have investigated the effect of a variety of solvents on the kinetics of this reaction and have also measured the rates of reaction with O_2 of a number of other stabilized carbon-centered radicals. For comparison, the kinetics of the reaction with O_2 of the unstabilized *tert*-butyl radical has also been examined. In addition we have measured, or attempted to measure, the rates of reaction with O_2 of several heteroatom-centered free radicals. For such species, the only kinetic result previously available was contained in a preliminary report from this laboratory on the reaction of oxygen with the tri-*n*-butyltin radical.[21]

Experimental Section

All experiments were carried out using laser flash photolytic techniques and employing for excitation the pulses from either a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ/pulse) or a Lumonics TE-860-2 excimer laser operated with Xe/HCl mixtures (308 nm, ~5 ns, up to 80 mJ/pulse). Transient absorptions were monitored with a computerized system having nanosecond response, which has been described previously.[22] Samples were contained in Suprasil cells made of 7 × 3 mm^2 (nitrogen laser) or 7 × 7 mm^2 (excimer laser) tubing. Mixtures of oxygen and nitrogen of precisely known composition were prepared using a Tylan mass flow gas controller–mixer system (reported accuracy ±0.1%). Typical flows through the controller were in the range 20–40 cm^3/min. A gas splitter system diverted a small fraction (~10%) of this flow through the sample in a fine stream of bubbles from a hypodermic needle. Particular care was taken to minimize the dead volume between the needle and controller and to ensure gas–liquid equilibration. The gas mixture was passed through the solution both before and during the actual experiment. Typically, the sample was exposed to 5–15 laser pulses at ca. 4-s intervals. Increasing or decreasing this interval, as well as changes in the number of laser pulses, was found not to affect the kinetic measurements. However, preliminary studies in which the samples were saturated before, but not during the experiment, led to results that were dependent on the number of, and interval between, the laser pulses. This indicated partial oxygen depletion in the region of the solution being examined and emphasizes the need to ensure gas–liquid equilibration and/or mixing of the solution.

The radicals studied were those which could be generated by the laser flash in an essentially instantaneous process, which gave well-characterized signals, and which decayed with simple first-order kinetics in the presence of oxygen (or were unaffected by oxygen). Commercially available radical precursors and solvents were purified by standard techniques. *tert*-Butyl phenylperacetate was prepared from *tert*-butyl hydroperoxide and phenylacetic acid in the usual way.[23]

Results

The measurement of the kinetics of the reaction of benzyl radicals with oxygen will be described in some detail to illustrate the general procedure that was followed. In this particular case, control experiments were carried out to show that the benzyl radical/O_2 kinetics did not depend on the radical source. Two precursors were used, 1,3-diphenylacetone and *tert*-butyl phenylperacetate, which yield benzyl according to the reactions:

$$PhCH_2COCH_2Ph \xrightarrow{h\nu} PhCH_2\dot{C}O + Ph\dot{C}H_2 \quad (3)$$

$$PhCH_2\dot{C}O \rightarrow Ph\dot{C}H_2 + CO \quad (4)$$

$$PhCH_2C(O)OOCMe_3 \xrightarrow{h\nu} Ph\dot{C}H_2 + CO_2 + Me_3CO\cdot \quad (5)$$

In these equations only species living 20 ns or more have been considered; i.e., the excited states of the precursors[24] and the $PhCH_2CO_2\cdot$ radical[25] have been ignored because they play no role in the kinetic analysis. The $PhCH_2\dot{C}O$ radical has a lifetime of 100–200 ns at room temperature.[28] The intermediacy of this radical can be ignored in the kinetic analysis provided the lifetime of the benzyl radical in the presence of oxygen has been "tuned", by the use of appropriately low oxygen concentrations, to be substantially longer than 200 ns.

Benzyl radicals decay by a combination of the reactions:

$$Ph\dot{C}H_2 + Ph\dot{C}H_2 \xrightarrow{2k_t} PhCH_2CH_2Ph \quad (6)$$

$$Ph\dot{C}H_2 + O_2 \xrightarrow{k_{Ox}} PhCH_2OO\cdot \quad (7)$$

In the absence of oxygen, the decay of the benzyl radicals, monitored at 317 nm,[29] follows remarkably clean second-order kinetics. For our studies it was more convenient to work under conditions where reaction 7 predominates. Reaction 6 and the other potential radical–radical reactions which destroy benzyl (such as reaction 8)

$$PhCH_2OO\cdot + Ph\dot{C}H_2 \rightarrow PhCH_2OOCH_2Ph \quad (8)$$

can therefore be ignored, and only first-order processes need to be taken into consideration. For this reason, our measurements at different oxygen concentrations usually exclude a value for $[O_2] = 0$. However, such a measurement was *always* carried out to ensure that the criterion of the predominance of reaction 7 over reaction 6 was met. Under these conditions the data should follow the equation:

$$k_{exptl} = k_0 + k_{Ox}[O_2] \quad (9)$$

where k_{exptl} $(=\tau^{-1})$ is the measured first-order rate constant for radical decay. The constant, k_0, includes all kinetically first-order

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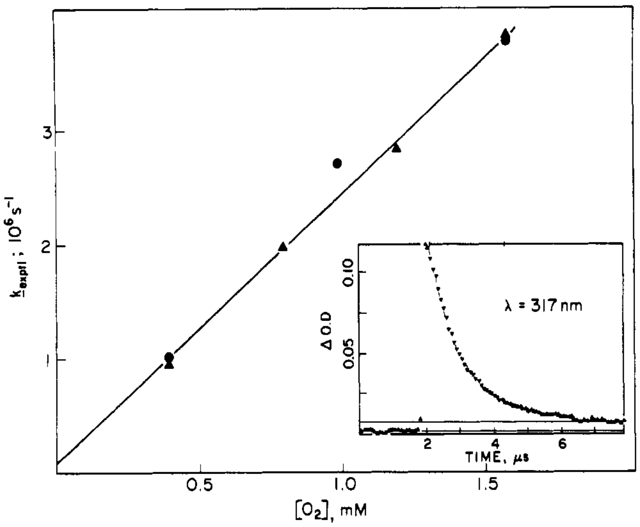

Figure 1. Determination of the rate constant for the reaction of benzyl radicals with oxygen in cyclohexane at 300 K, according to eq 9, using 1,3-diphenylacetone (▲) or $PhCH_2C(O)OOCMe_3$ (●) as radical precursors. Insert: Representative decay trace for $[O_2] = 3.97 \times 10^{-4}$ M, obtained using the ketone precursor.

decay processes other than the reaction with oxygen, as well as terms reflecting reversibility (see below), and k_{Ox} refers only to the forward reaction. The kinetically first-order decay processes, which could include, for example, reaction with the solvent, are expected to be relatively unimportant; i.e., $k_0 \sim 0$. Figure 1 shows a typical plot made according to eq 9, the inset being a representative decay trace for the $Ph\dot{C}H_2$ radical. The correlation coefficient for the plot in this figure has a value of 0.9947, which is an intermediate rather than an exceptional value. Only one measurement in this work led to a correlation coefficient ≤0.98 (see supplementary material).

Oxygen concentrations in solution were based on reported solubilities[30] at 298 or 300 K and were corrected to allow for the vapor pressure of the solvent (see "Explanation of the Tables" in the supplementary material). Any difference in solubility between 298 and 300 K was ignored, and no corrections were introduced to allow for solute effects on the sample's vapor pressure or for day-to-day variations in atmospheric pressure.

The kinetic results of the present study are summarized in Table I for those radicals which reacted with O_2 at a measurable rate. Full kinetic details are provided as supplementary material in Tables II–XIII. It should be noted that the laser technique measures the rate constants for radical scavenging by oxygen, but provides no information concerning the mechanism of the reaction. Furthermore, the k_{exptl} values obtained actually represent the difference between the forward and reverse reactions; i.e., they are really $k_{Ox}[O_2] - k_{-Ox}$. However, when the data are plotted against $[O_2]$, the value of k_{Ox} refers only to the forward process. Further, the reactions of the radicals listed in Table I are not expected to be significantly reversible under our conditions (see Discussion).

The *tert*-butyl radicals were generated by photolysis of di-*tert*-butyl ketone:

$$Me_3CCOCMe_3 \xrightarrow{h\nu} Me_3\dot{C} + Me_3C\dot{C}O \qquad (10)$$

They were characterized by their UV spectrum[31] and were monitored at 320 nm. The pivaloyl radical, $Me_3C\dot{C}O$, which is formed simultaneously with the *tert*-butyl radical, is known[32] to undergo decarbonylation at a rate which is slow in relation to the time scale of our experiment. It does not, therefore, intefere with the kinetic analysis. The 2-hydroxyprop-2-yl radicals were generated by the photolysis of acetone in 2-propanol viz.:

$$MeCOMe \xrightarrow{h\nu} (MeCOMe)^* \qquad (11)$$

$$(MeCOMe)^* + Me_2CHOH \rightarrow 2Me_2\dot{C}OH \qquad (12)$$

and were characterized by their UV spectrum[33] and monitored at 355 nm. All the other radicals listed in Table I were generated by hydrogen-atom abstraction from appropriate precursors using *tert*-butoxyl radicals photogenerated from di-*tert*-butyl peroxide. These reactions are all sufficiently rapid[21,34–37] that radical generation can be formally regarded as an instantaneous process. The spectra of all these radicals are known[21,33–37] and the monitoring wavelengths were chosen accordingly. In a few other systems that were examined the rate constants for the radical's reaction with oxygen could not be measured. Some details of these experiments are given below.

Somewhat to our surprise,[38] the diphenylaminyl radical, $Ph_2N\cdot$, was unreactive toward oxygen within the time scale of our experiments. This radical was generated by reaction of *tert*-butoxyl with diphenylamine. The spectrum of the transient which was formed agreed well with what literature data are available for the $Ph_2N\cdot$ radical,[46–48] there being a strong maximum at 400 nm and a weaker maximum at 550 nm. The transient decayed in a few microseconds, which rules out the highly persistent $Ph_2N\dot{O}$ radical, and was formed too rapidly in degassed solutions to be the (unknown) $Ph_2NOO\cdot$ radical. The transient could not be scavenged in the time scale monitored (up to 80 μs) even when the solution was saturated with 100% oxygen. We conclude that if the $Ph_2N\cdot$ radical does react with O_2, the rate constant for this process must be less than 10^7 M^{-1} s^{-1}. Exploratory experiments in which the phenoxyl radical was generated by reaction of *tert*-butoxyl with phenol showed that it too was unreactive toward oxygen on our time scale.[52]

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(52) The highly persistant 2,4,6-tri-*tert*-butylphenoxyl radical reacts with O_2. The products have been identified.[53,54] The reaction is first order in O_2 and second order in phenoxyl radical.[55] The rate constant for reaction can be described by the relation by $(k/M^{-2}\ s^{-1}) = (-14.5 \pm 0.9) + (27.2 \pm 1.4)/\theta$ where $\theta = 2.3RT$ kcal/mol.[55]

The transient spectra obtained by *tert*-butoxyl attack on diethoxyphenylphosphine, 1,4-pentadiene, and methyl linoleate were all too weak for detailed kinetic studies. Cumyl radicals were produced by the photodecomposition of azocumene. There appeared to be other transients formed which underlay the cumyl radical signal and interfered with the accurate monitoring of the cumyl–oxygen reaction.[56] However, it was clear that cumyl reacts with oxygen at a rate which is equal to, or not less than 75% of, the rate of the benzyl–oxygen reaction.

Discussion

Our results show that the rate constants for the reactions of carbon-centered radicals with oxygen are not entirely insensitive to the nature of the radical, but that such sensitivity is rather small (see Table I). In particular, the rate for the reaction of the resonance-stabilized benzyl radical with oxygen is not very different from the rate for the reaction of the nonstabilized[57] *tert*-butyl radical. It seems probable that previous reports that benzyl and benzylic radicals react with oxygen relatively slowly reflect poor equilibration of the system with oxygen, thus leading to partial oxygen depletion in the solution. Indeed, in some of our preliminary work we found that this could become a critical problem, easily leading to errors of one or even two orders of magnitude in the calculated rate constant. Naturally, oxygen equilibration is particularly important in flash experiments since relatively large radical concentrations are produced in a short time.

We do not wish to imply that all carbon-centered radicals react with oxygen at the same rate; clearly they do not. The resonance-stabilized radicals react with oxygen at rates which are noticeably slower than rates found for the nonstabilized radicals. A similar phenomenon has been observed by Hasegawa and Patterson[14] in a study of the reaction with oxygen of some carbon-centered radicals derived from fatty acids.

The reactions with oxygen of radicals that are highly resonance stabilized, such as triphenylmethyl[58–60] and some pentadienyls derived from fatty acids,[61–63] are known to be reversible even at room temperature. The reactions of nonstabilized radicals, such as *tert*-butyl,[64] with oxygen are irreversible even at quite elevated temperatures. The importance of this peroxyl radical β-scission process,

$$\text{ROO}\cdot \xrightarrow{k_{-\text{Ox}}} \text{R}\cdot + \text{O}_2 \qquad (-1)$$

in autoxidation and combustion has been emphasized by Benson.[65] Equilibrium constants for reaction 1 can be calculated for carbon-centered radicals of known stabilization energy.[65,66] For example, for the cumyl radical at 300 K Nangia and Benson[66] have estimated that $\Delta S°_1 = 25.8$ cal mol^{-1} K^{-1} and $\Delta H°_1 = 20.2$ kcal/mol, which yield $K_1 = 8 \times 10^{-10}$ M. Taking k_{Ox} to be 3×10^9 M^{-1} s^{-1} at this temperature yields a $k_{-\text{Ox}}$ value of 2.4 s^{-1}. This rate constant was subsequently measured by Howard et al.[67] and found to be ca. 2 s^{-1} at 303 K. Even the more highly resonance-stabilized 1,1-diphenylethyl radical has a k_{-1} value of only ca. 1.7×10^3 s^{-1} at 303 K.[68] It would therefore appear that for benzyl and the other carbon-centered radicals studied in this work the reversibility of reaction 1 is unimportant on the time scale of our experimental measurements of k_{Ox}.

The reactions of benzyl radicals with oxygen are somewhat slower in solvents of low viscosity than would be expected for diffusion-controlled process.[69] The reaction tends to become diffusion-controlled in the more viscous solvents. Thus, comparing only the saturated hydrocarbon solvents, hexane, cyclohexane, and hexadecane, the k_{Ox} are 2.78, 2.36, and 1.04×10^9 M^{-1} s^{-1}, respectively; the viscosities (at 293 K)) are 0.31, 0.98, and 3.34 cP, respectively. Solvent polarizability, polarity, and ability to hydrogen bond have essentially no effect on k_{Ox} values: e.g., benzene, $k_{\text{Ox}} = 2.88 \times 10^9$ M^{-1} s^{-1}, $\eta_{298} = 0.65$ cP; acetonitrile, $k_{\text{Ox}} = 3.42 \times 10^9$ M^{-1} s^{-1}, $\eta_{298} = 0.36$ cP; 2-propanol, $k_{\text{Ox}} = 2.51 \times 10^9$ M^{-1} s^{-1}, $\eta_{293} = 2.86$ cP.

For some carbon-centered radicals the reaction with oxygen may yield the hydroperoxyl radical rather than the peroxyl radical corresponding to a simple addition of oxygen. From product studies this is known to be the case for the cyclohexadienyl radical.[70,71]

$$\text{C}_6\text{H}_7\cdot + \text{O}_2 \rightarrow \text{C}_6\text{H}_6 + \text{HOO}\cdot \qquad (13)$$

This reaction apparently involves a direct abstraction of the H atom.[72] However, the products are determined by the fact that the oxygen addition process,

$$\text{C}_6\text{H}_7\cdot + \text{O}_2 \rightleftarrows \text{C}_6\text{H}_7\text{OO}\cdot \qquad (14)$$

is probably reversible under autoxidation conditions.[72] Our measured value of k_{Ox} for cyclohexadienyl represents the sum of the rate constants for all forward reactions, regardless of mechanism.

A similar uncertainty applies to the reactions with oxygen of the $(\text{C}_2\text{H}_5)_2\text{N}\dot{\text{C}}\text{HCH}_3$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals. Thus, it has been shown by kinetic analysis and by radical trapping experiments that HOO· is the major chain carrying peroxyl radical in the autoxidation of triethylamine.[73] There is also experimental evidence for the participation of HOO· as a chain carrying radical in alcohol autoxidations.[74–76] Our kinetic data for these radicals do not distinguish addition and H-atom abstraction by oxygen.

The rate constant for the reaction of *n*-Bu$_3$Sn· with O$_2$, 7.5×10^9 M^{-1} s^{-1}, is larger than the value reported previously;[21] probably there was poor gas–liquid equilibration in the earlier experiments. The high k_{Ox} value for *n*-Bu$_3$Sn· contrasts with the k_{Ox} value of 2.5×10^9 M^{-1} s^{-1} found for *n*-Bu$_3$Ge· (which is similar to the values found for carbon-centered radicals). It seems unlikely that this difference could be related to the unusual structure with two magnetically equivalent oxygen atoms which has been assigned to the tri-*n*-butylstannylperoxyl radical on the basis of its EPR spectrum.[77,78] We suggest that heavy atom effects due to the tin lead to a relaxation of the "one-third" spin selection rule applicable to radical–oxygen interactions.[69]

Finally, we note that, with the exception of a few recent measurements using time-resolved techniques, most kinetic studies

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of the reactions of carbon-centered radicals with oxygen have yielded k_{Ox} values that are lower, often considerably lower, than the correct values. Conclusions and any other rate constants that have been based on "low" k_{Ox} values may require substantial revision.

Note Added in Proof. A direct determination of the equilibrium constant and thermodynamic parameters for the gas-phase reaction, allyl + $O_2 \rightleftharpoons$ allylperoxyl, have recently been reported.[79]

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Registry No. $PhCH_2\cdot$, 2154-56-5; $Me_3C\cdot$, 1605-73-8; c-$C_6H_7\cdot$, 12169-67-4; $(C_2H_5)N\dot{C}HCH_3$, 26374-14-1; $CH_3\dot{C}(OH)CH_3$, 5131-95-3; *n*-$Bu_3Ge\cdot$, 55321-84-1; *n*-$Bu_3Sn\cdot$, 20763-88-6; O_2, 7782-44-7.

Supplementary Material Available: Tables II–XIII giving detailed kinetic data (7 pages). Ordering information is given on any current masthead page.

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Secondary Isotope Multiplet NMR Spectroscopy of Partially Labeled Entities. Carbon-13 SIMPLE NMR of Carbohydrates

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Abstract: ^{13}C NMR measurements have been made in Me_2SO-d_6 solutions of some carbohydrates (methyl α-D-gluco- and galactopyranosides, melibiose, maltose, and β-cyclodextrin) in which exchangeable protons have been partially deuterated. Signals from single carbon atoms are observed as a series of multiplets (singlets to octets) with intensity ratios that vary quantitatively with OH:OD ratios. Partial deuteration of exchangeable protons in molecules permits direct observation of the different isotopomers measured under conditions of slow exchange and the resonance line separations can be analyzed in terms of the two-bond (β) and three-bond (γ) isotope effects that contribute to the deuterium-induced secondary isotope shift. Magnitudes of β and γ effects are found to vary with configuration of carbon atoms, and substitution and hydrogen bonding of hydroxyl groups. Signal multiplets and magnitudes of isotope effects are used to assign the spectra of carbohydrates as shown for both α- and β-forms of the $\alpha 1 \rightarrow 6$-linked (melibiose) and $\alpha 1 \rightarrow 4$-linked (maltose) reducing disaccharides. The method also confirms the presence and direction of intramolecular hydrogen bonding in $\alpha 1 \rightarrow 4$ glucosides (i.e., C2′–O2′⋯H–O–C3) by observation of an isotope effect on C2′ transmitted through a hydrogen bond. Measurements by NMR spectroscopy of secondary isotope multiplets of partially labeled entities (SIMPLE NMR) have widespread application for signal assignment and for studying isotope effects in molecules.

Isotope effects are well-established in NMR spectroscopy.[1] Primary isotope shifts have not been extensively studied because access to multinuclear NMR spectroscopy would normally be required; e.g., for the hydrogen atom the primary isotope shift $[\delta({}^{n}H) - \delta({}^{1}H), n = 2, 3]$ is determined by results of ^1H, ^2H, and/or ^3H NMR spectroscopy[2] of isotopically labeled species (isotopomers). A secondary isotope shift, $\delta(X^{n}H) - \delta(X^{1}H)$, is observed in isotopomers by NMR spectroscopy of the X nucleus ($X = {}^1H$, ^{13}C, etc.). More work has been done with secondary isotope shifts because measurement, although depending on the availability of isotopomers, is achieved by observation of the secondary nucleus X. Use of the latter phenomenon is greatly facilitated if isotopic replacement is readily accomplished as with exchangeable protons, e.g., OH, NH, and SH groups, and application of the method depends on whether the protons are in fast or slow exchange.[3-7] For example, Feeney and co-workers[3] demonstrated that deuterium isotope effects could be observed by ^{13}C carbonyl resonances in peptides with slowly exchanging vicinal N–D bonds in a 50:50 H_2O–D_2O solution whereas Grant and co-workers[4] showed that the isotope effect can be used to differentiate between carbonyl groups associated with rapidly exchanging OH groups and those associated with slowly exchanging amide NH groups. Indeed, when the rate of proton exchange of amides in dipolar aprotic solvents is slowed down, resolution of individual $^{13}C{=}O$ signals corresponding to the $O{=}CNH_2$, $O{=}CNHD$, and $O{=}CND_2$ species is possible.[5] Similar work was attempted with carbohydrates by Vincendon and co-workers[6,7] where the hydroxyl group exchange rate was slowed down by working in dimethyl sulfoxide (Me_2SO-d_6) and the consequent broadening of carbon atoms substituted with hydroxyl groups served to identify them, though no information was derived to enable individual C–OH resonances to be assigned.

Assignment of ^{13}C NMR signals of carbohydrates[8] may be made by chemical substitution or empirical correlations[9-11] by

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