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

		C1	C2	C3	C4	C5	C6
α-D-glucopyranose (**1**)		$\beta\gamma$	$\beta\gamma_2$	$\beta\gamma_2$	$\beta\gamma$	γ_2	β
	Δ_β	97	108	99	104		117
	Δ_γ	*b*	39	43	36	23	
β-D-glucopyranose (**2**)		$\beta\gamma$	$\beta\gamma\gamma'$	$\beta\gamma_2$	$\beta\gamma$	γ_2	β
	Δ_β	104	101	100	100		117
	Δ_γ	17	34; 67	45	31	23	
methyl α-D-glucopyranoside (**3**)		γ	$\beta\gamma$	$\beta\gamma_2$	$\beta\gamma$	γ_2	β
	Δ_β		107	102	104		117
	Δ_γ	17	35	44	36	25	
β-cellobiose (**4**)							
β-D-glucopyranosyl		γ	$\beta\gamma$	$\beta\gamma_2$	$\beta\gamma$	γ_2	β
	Δ_β		105	94	93		112
	Δ_γ	17	28	44	31	24	
β-D-glucopyranose		$\beta\gamma$	$\beta\gamma\gamma'$	$\beta\gamma$	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	$\beta\gamma$	$\beta\gamma_2$	$\beta\gamma$	γ_2	β
	Δ_β		102	100	101		115
	Δ_γ	*b*	34	40	36	20	
β-D-fructofuranose		β	$\gamma\gamma'$	$\beta\gamma_2$	$\beta\gamma$	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.

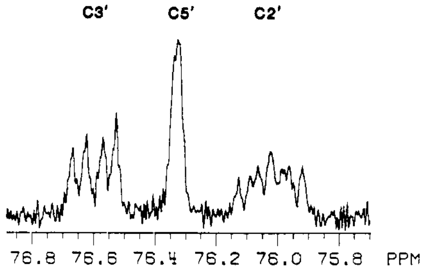

Figure 2. 75.8–76.8 ppm region of the proton-decoupled carbon-13 NMR spectrum of β-cellobiose (**4**) with partially deuterated hydroxyls (R = 0.86).

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 $\beta\gamma\gamma'$, whereas the second, C3′, has only one hydroxylated neighbor (C2′) and is of type $\beta\gamma$.

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

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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.

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

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

$$\text{and} \qquad H_2O_2 + 2H^+ + R \rightarrow P + 2H_2O \tag{3}$$

When $E_1{}^{\circ\prime} \leq E_{\text{cat}}{}^{\circ\prime}$, 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

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of a catalyst, tetrakis[4-*N*-methylpyridyl or 4-pyridyl]porphinecobalt(III) ($Co^{III}TMPyP$ or $Co^{III}TPyP$), either dissolved in the solution or strongly adsorbed[1,2] on a glassy carbon or graphite electrode. Such a catalytic cathode in a divided cell (glass frit or NaFion membrane) produced H_2O_2 with an average yield of 93.7 ± 2.2% from an air-saturated 0.05 M H_2SO_4 catholyte. Values of E_{cat} between −0.1 and +0.2 V (referenced to a saturated KCl silver–silver chloride electrode) were employed. The amount of H_2O_2 produced was quantitated by titration with $KMnO_4$.[3]

The oxidation of I^- to I_2 illustrates the matching of the cathode and anode to produce the same product with 200% yield. The anolyte contained 0.5 M H_2SO_4 and 0.1 M KI. The H_2O_2 was generated catalytically from air-saturated H_2SO_4 and was then was reacted with an excess of KI. The I_2 formed was quantitated by titration with thiosulfate.[4] An average yield for I_2 was 194 ± 3% (anode, 101 ± 1%; cathode; 93 ± 3%). Br_2 could be similarly generated from Br^-. Yields were independent of the applied cathodic potential between −0.2 and +0.2 V. When the potential became more negative than −0.20 V, the yield decreased, possibly due to H_2O_2 reduction at the cathode.

Two different electrosynthetic conversions, As(III) to As(V) and the bromination of cyclohexene, were attempted, each relying on the ability to generate I_2 or Br_2 as a reagent. Since the oxidation of As(III) is electrochemically irreversible at most electrodes,[5-7] it was accomplished indirectly through the generation of Br_2 (or I_2) at the anode and H_2O_2 catalytically at the cathode. The average total yield of As(V) was 155 ± 5% (anode, 95 ± 1%; cathode, 60 ± 5%). The catholyte contained 0.02 M $HAsO_2$ in 0.5 M H_2SO_4, and the anolyte 0.02 M $HAsO_2$ in 0.5 M H_2SO_4 and 0.4 M KBr. The charge passed through the cell varied from 20 to 45 C for each run. The yield was determined by analyzing for the unreacted As(III) remaining by iodometric titration.[8] The presence of As(V) has no effect on the yield while the addition of KBr (0.4 and 1.3 M) to the cathodic compartment increased the yield (cathode, 77% and 89%, respectively). This increase is believed to be due to the H_2O_2, which, besides oxidizing As(III) to As(V), also oxidizes Br^- to Br_2, which in turn oxidizes As(III). Although the rate for the reaction between H_2O_2 and Br^- is relatively slow,[9] the large excess of Br^- competes favorably to circumvent the loss of H_2O_2 through disproportionation. Thus, yields approaching 200% appear feasible.

In the case of cyclohexane bromination, it was necessary to transfer the Br_2 generated in both compartments to an external reaction vessel containing cyclohexene. This transfer was made by passing an air stream through the anolyte during electrolysis. In the catholyte (0.5 M H_2SO_4) O_2 was bubbled through the solution during electrolysis for conversion to H_2O_2, and solid KBr was added after the electrolysis was stopped. The Br_2 formed was then transferred via an air stream to a second external reactor containing cyclohexene dissolved in CCl_4 and maintained at ice temperature. After CCl_4 was evaporated, the residue was dissolved in ethanol and subjected to gas chromatographic analysis; 1% DMF in ethanol served as an internal reference. The average total yield of dibromocyclohexane was 148 ± 5% (anode, 87 ± 2%; cathode, 61 ± 6%). The lower cathodic yield may reflect a loss of H_2O_2 during the generation period and/or a lower efficiency of the H_2O_2–Br^- reaction rather than an inefficiency in the Br_2 transfer and reaction with cyclohexene. Nonetheless, the yield was significantly increased above a conventional cell utilizing only the anodic compartment.

There have been reports in which both anodic and cathodic reactions have been matched to yield a single product. For example, NaOH, generated from the cathodic compartment of a chlor-alkali cell, can be reacted with the anodically generated Cl_2 to produce sodium hypochlorite or, through further oxidation, sodium chlorate.[10] Two other "matched" electrosynthetic schemes have been also recently reported.[11,12] However, the matching of *both* cell compartments to produce the same product from a common reactant has not been previously reported or demonstrated. Experiments are underway to explore the full scope and applicability of the concept.

Acknowledgment. We gratefully acknowledge the support of this work by a grant from Koppers Co., Inc., Pittsburg, PA.

Registry No. H_2O_2, 7722-84-1; O_2, 7782-44-7; I^-, 7681-11-0; Br, 24959-67-9; Br_2, 7726-95-6; I_2, 7553-56-2; $HAsO_2$, 13768-07-5; H_3AsO_4, 7778-39-4; KBr, 7758-02-3; $Co^{III}TMPgP$, 51329-41-0; $Co^{III}TPyP$, 61136-56-9; cyclohexene, 110-83-8; dibromocyclohexane, 52590-61-1.

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Carbon-14 Kinetic Isotope Effects and Kinetic Studies in the Syn-Elimination Reactions of (2-Phenylethyl)dimethylamine Oxides[1]

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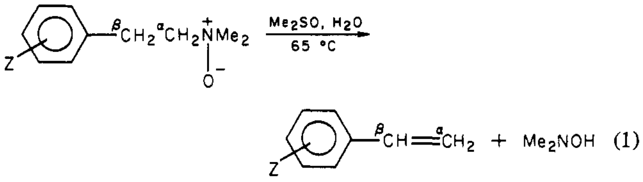
Received January 24, 1983

As the first reported example of a carbon isotope effect in a clearly established syn-elimination reaction, we have found that there are large carbon-14 kinetic isotope effects in the thermal decomposition of both α- and β-carbon-14 labeled (2-phenylethyl)dimethylamine oxides (eq 1). The effects of substituents on the rates of the reactions for Z = *p*-CH_3O, *p*-CH_3, H, and *p*-Cl have also been investigated.



$$k/^{\alpha}k = 1.061 \pm 0.006 \qquad k/^{\beta}k = 1.036 \pm 0.005$$

All of the reaction systems for which carbon isotope effect data[2-4] have been reported to date[2] by our research group[3] and that of Saunders[4] have had E2 mechanisms with varying degrees

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(1) This work was supported by the National Science Foundation.

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