

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 -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)		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.

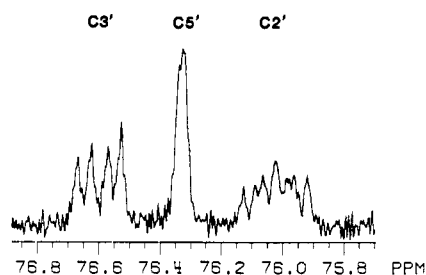


Figure 2. 75.8-76.8 ppm region of the proton-decoupled carbon-13 NMR spectrum of β -cellobiose (4) with partially deuterated hydroxyls ($R = 0.86$).

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 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 $\Delta_\beta(\text{C}_6) > \Delta_\beta(\text{C}_2) > \Delta_\beta(\text{C}_4) \approx \Delta_\beta(\text{C}_3)$ and $\Delta_\gamma(\text{C}_2, \text{trans anomeric OH}) > \Delta_\gamma(\text{C}_3) > \Delta_\gamma(\text{C}_2) \approx \Delta_\gamma(\text{C}_4) > \Delta_\gamma(\text{C}_5) > \Delta_\gamma(\text{C}_1)$. 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.

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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.

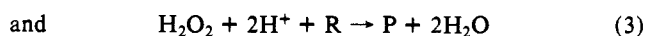
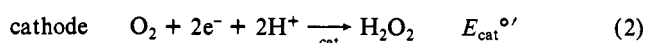
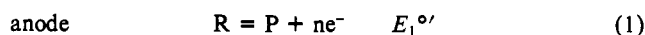
A 200% Efficient Electrolysis Cell

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We report the concept and experimental demonstration of an electrochemical scheme in which a common reactant is oxidized to the same product in both the anodic and cathodic compartments of an electrolysis cell. Thus, the product 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 in eq 1-3. Essential to this scheme is the identity of product, P, produced in both reactions 1 and 3.



When $E_1^{o'} \leq E_{\text{cat}}^{o'}$, 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

of a catalyst, tetrakis[4-*N*-methylpyridyl or 4-pyridyl]porphine-cobalt(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 H₂O₂ with an average yield of 93.7 ± 2.2% from an air-saturated 0.05 M H₂SO₄ 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 H₂O₂ produced was quantitated by titration with KMnO₄.³

The oxidation of I⁻ to I₂ illustrates the matching of the cathode and anode to produce the same product with 200% yield. The anolyte contained 0.5 M H₂SO₄ and 0.1 M KI. The H₂O₂ was generated catalytically from air-saturated H₂SO₄ and was then reacted with an excess of KI. The I₂ formed was quantitated by titration with thiosulfate.⁴ An average yield for I₂ was 194 ± 3% (anode, 101 ± 1%; cathode; 93 ± 3%). Br₂ 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 H₂O₂ 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 I₂ or Br₂ 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 Br₂ (or I₂) at the anode and H₂O₂ 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 HAsO₂ in 0.5 M H₂SO₄, and the anolyte 0.02 M HAsO₂ in 0.5 M H₂SO₄ 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 H₂O₂, which, besides oxidizing As(III) to As(V), also oxidizes Br⁻ to Br₂, which in turn oxidizes As(III). Although the rate for the reaction between H₂O₂ and Br⁻ is relatively slow,⁹ the large excess of Br⁻ competes favorably to circumvent the loss of H₂O₂ through disproportionation. Thus, yields approaching 200% appear feasible.

In the case of cyclohexene bromination, it was necessary to transfer the Br₂ 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 H₂SO₄) O₂ was bubbled through the solution during electrolysis for conversion to H₂O₂, and solid KBr was added after the electrolysis was stopped. The Br₂ formed was then transferred via an air stream to a second external reactor containing cyclohexene dissolved in CCl₄ and maintained at ice temperature. After CCl₄ 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 H₂O₂ during the generation period and/or a lower efficiency of the H₂O₂-Br⁻ reaction rather than an inefficiency in the Br₂ 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 Cl₂ 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.

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Registry No. H₂O₂, 7722-84-1; O₂, 7782-44-7; I⁻, 7681-11-0; Br₂, 24959-67-9; Br₂, 7726-95-6; I₂, 7553-56-2; HAsO₂, 13768-07-5; H₃AsO₄, 7778-39-4; KBr, 7758-02-3; Co^{III}TMPyP, 51329-41-0; Co^{III}TPyP, 61136-56-9; cyclohexene, 110-83-8; dibromocyclohexane, 52590-61-1.

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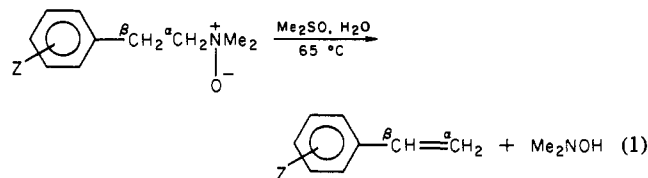
Carbon-14 Kinetic Isotope Effects and Kinetic Studies in the Syn-Elimination Reactions of (2-Phenylethyl)dimethylamine Oxides¹

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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



$$k/\alpha k = 1.061 \pm 0.006 \quad k/\beta k = 1.036 \pm 0.005$$

on the rates of the reactions for Z = *p*-CH₃O, *p*-CH₃, H, and *p*-Cl have also been investigated.

All of the reaction systems for which carbon isotope effect data²⁻⁴ have been reported to date² by our research group³ and that of Saunders⁴ have had E2 mechanisms with varying degrees

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

(2) Fry, A. *Chem. Soc. Rev.* 1972, 1, 163-210. References to earlier heavy-atom isotope effect studies of elimination reaction mechanisms are to be found in this review.

(3) For a current brief review of our experimental work, see: Fry, A.; Sims, L. B.; Eubanks, J. R. I.; Hasan, T.; Kanski, R.; Pettigrew, F. A.; Crook, S. "Proceedings of the International Symposium on the Synthesis of Appl. Isotopically Labeled Compounds"; Duncan, W. P., Susan, A. B., Eds.; Elsevier: Amsterdam, 1983; pp 133-138. Lewis, D. E.; Sims, L. B.; Yamataka, H.; McKenna, J. J. *Am. Chem. Soc.* 1980, 102, 7411-7419. Burton, G. W.; Sims, L. B.; McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* 1977, 1847-1853. Hasan, T.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.*, in press. Eubanks, J. R. I. Ph.D. Dissertation, University of Arkansas, 1981. Pettigrew, F. A. Ph.D. Dissertation, University of Arkansas, 1981.

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