# Oxidation of 2-Propanol to Acetone by Dioxygen on a Platinized Electrode under **Open-Circuit Conditions**<sup>1</sup>

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This paper examines the catalytic oxidation of 2-propanol by dioxygen on a platinized platinum gauze electrode. Under open-circuit conditions, the rate of reaction was limited by mass transport of dioxygen to the catalyst surface and obeyed the rate law  $-d[ROH]/dt = k[ROH]^0[Pt_s]^1 P_{O_2}^{-1}$ . The rate of reaction depended on the rate of stirring of the system. No kinetic deuterium isotope effect was observed upon substitution of 2-propanol- $d_7$  for 2-propanol- $d_0$ . Under the reaction conditions employed, the open-circuit potential of the catalyst during the catalytic oxidation of 2-propanol indicated that the platinum surface was covered predominately with platinum hydride and not with platinum oxide. No catalyst deactivation due to reaction of dioxygen with surface platinum atoms was observed, and hydrogen peroxide could be substituted for dioxygen as the oxidizing agent in the reaction. The reaction is proposed to proceed by the formation of an intermediate surface alkoxide that dehydrogenates and produces acetone and surface hydrides. These surface hydrides then react with dioxygen, hydrogen peroxide, platinum oxide, or some other oxidizing species and yield (ultimately) water, possibly by an electrochemical local cell mechanism.

### Introduction

The catalytic oxidation of organic compounds with dioxygen is widely used in synthesis.<sup>3</sup> The heterogeneous platinum- or palladium-catalyzed oxidation of alcohols with dioxygen to aldehydes, ketones, and/or carboxylic acids in the liquid phase is a highly useful, if nonrepresentative, example of this class of reactions. This process has proved particularly valuable in oxidative transformations of carbohydrates as a result of its high regioselectivity.4-8

Primary alcohols are readily oxidized to carboxylic acids in aqueous basic solution and in lower yield to aldehydes in neutral or acidic aqueous solution or in organic solvents. Secondary alcohols are oxidized to the corresponding ketones. Primary hydroxyl groups are oxidized preferentially in the presence of secondary hydroxyl groups. Axial groups on cyclohexane rings oxidize more rapidly than equatorial hydroxyl groups. Carboncarbon double bonds do not oxidize or isomerize.

Various mechanisms have been proposed for the oxidation of alcohols on platinum catalysts: dehydrogenation of the substrate on the catalyst surface and reaction of the resulting surface hydrogen atoms with oxygen to produce water,9-11 oxidation via a radical chain mechanism in solution initiated by reaction of the

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substrate with the catalyst surface,<sup>12</sup> or reaction of the alcohol with oxygen adsorbed on the surface of the catalyst.<sup>13,14</sup>

Platinum is either used in the form of platinum black (Adam's catalyst) or dispersed on supports such as carbon, alumina, or silica gel.<sup>5-7</sup> Oxidations have been successfully performed in water, *n*-heptane, acetone, 2-butanone, and dioxane.<sup>6</sup> The major disadvantage of the platinum-catalyzed oxidation of alcohols is the short lifetime of the catalyst as it is ordinarily used. The amount of platinum catalyst commonly used in oxidations of carbohydrates is 10-20 wt % of the quantity of substrate to be oxidized.<sup>5</sup> Oxidations carried out using low concentrations of dioxygen show longer catalyst lifetimes.<sup>15</sup> Although the nature of the processes poisoning the catalyst have not been established in detail, the observation that reactions conducted at high partial pressures of dioxygen may show short catalyst lifetimes suggests some oxidative process occurring at the catalyst surface. Other factors that might contribute to the poisoning of the catalyst include overoxidation of substrates to side-products that act as catalyst poisons and inhibition of reaction due to adsorption of the reaction product on the catalyst surface.

This paper describes a study of the platinum-catalyzed oxidation of 2-propanol to acetone in aqueous solution. Its objectives were to clarify the mechanism of the reaction, to establish the processes responsible for catalyst deactivation, and to suggest reaction protocols that would make it possible to use this type of reaction with greater practicality by extending the catalyst lifetime.

The work is based on an experimental strategy in which the working catalyst could be interrogated while operating using electrochemical techniques to infer the character of its surface. We constructed an electrochemical cell with which it was possible to monitor the open-circuit potential of the catalyst (the catalyst potential with no applied current or voltage relative to a standard potential) under active reaction conditions. The system was a compromise between catalytic and electrochemical requirements.

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Figure 1. Two-compartment electrochemical cell used to study the oxidation of 2-propanol by oxygen on a platinized platinum gauze electrode.

To achieve useful rates of catalytic production of products, we used a catalyst having a relatively high (for an electroanalytical system) surface area. With this system, mass transport of reactants to and products from the surface of the electrode/catalyst was not well-defined, and the distribution of electrochemical potential across the catalyst surface was probably not uniform. Both the surface area of the system and its dispersion (that is, the fraction of platinum atoms present at the surface) were low and not entirely representative of catalysts used in synthetic practice. Despite these compromises, however, the system provided information that made possible a clear definition of major features of the reaction.

### Results

Reactions were run in a two-compartment electrochemical cell (Figure 1). The platinum catalyst/electrode was a section of 80-mesh platinum gauze that was rolled into a cylinder and then platinized.<sup>16</sup> This electrode had a geometric surface area of 160 cm<sup>2</sup> and a real surface area of  $5.7 \times 10^4$  cm<sup>2</sup> ( $1.2 \times 10^{-4}$  mol of Pt), determined from anodic galvanostatic charging curves.<sup>16,17</sup> A description of the electrochemical cell and procedures used for electrode preparation and characterization are available as supplementary material (see the paragraph at the end of the paper).

Oxidations of 1.20-mmol aliquots of 2-propanol were run in 6.0 mL of 0.20 N  $H_2SO_4$  at 1.0 atm of  $O_2$  unless otherwise noted; a total of 40 such oxidations were performed with no evidence of poisoning or loss of activity of the catalyst. The solution in the working electrode compartment was replaced on completion of each reaction. The productivity (PROD<sub>5</sub>, eq 1) for this catalyst/electrode was 400 when the series of 40 reactions was terminated.

$$PROD_{s} = \frac{\text{mol of 2-propanol oxidized}}{\text{mol of surface platinum}}$$
(1)

Over the course of the first six of these oxidations, the reaction rate at a constant stirring rate decreased slightly; for the remainder of the oxidations, the reaction rates measured at constant stirring rates were very reproducible. After the sequence of reactions had been completed, the cell was disassembled and the surface area of the working electrode remeasured. The measured value was

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 $4.8 \times 10^4$  cm<sup>2</sup>, a decrease in surface area of ca. 15% from that originally measured after preparation of the catalyst electrode.

Dependence of Rate of Oxidation on the Rate of Stirring. The rate of oxidation of 2-propanol increased with increasing rate of stirring ( $\omega$ ) of the platinized electrode catalyst at 1.0 atm of O<sub>2</sub>, suggesting that the reaction was mass transport-limited. Stirring rates above 1000 rpm could be used only for very short periods of time before damage to the bearing and stirring rod resulted. For stirring rates up to 1000 rpm, the surface of the solution appeared fairly quiescent and no vortexing was observed; at 1700 rpm, vortexing was pronounced and the rate of reaction increased dramatically.

Plotting the log of reaction rate versus log  $\omega$  for oxidations run at 220, 440, and 850 rpm indicated that the dependence of the reaction on the rate of stirring was

$$-d[ROH]/dt \propto \omega^{0.64\pm0.08}$$
(2)

For rotating disk electrodes, the rate of reaction varies as  $\omega^{0.5}$  under laminar flow conditions and as  $\omega^{0.8-0.95}$  under turbulent flow conditions.<sup>18</sup> It is not possible to calculate rates of mass transport to the geometrically complex catalyst/electrode employed in this work, but the observed exponent is in a plausible range.

Dependence of Reaction Rate on the Pressure of Dioxygen. These data were obtained at a constant stirring rate of 900 rpm and at four partial pressures of dioxygen (0.23, 0.46, 0.75, and 1.00 atm). The partial pressure of dioxygen was adjusted by mixing dioxygen with argon, and the gas mixture was passed over the surface of the stirred solution at ca. 45 mL min. The gas pressure over the solution was always 1.0 atm. The reaction rate at two different partial pressures of dioxygen were checked during the oxidation of one 1.20-mmol aliquot of 2-propanol: the reaction was monitored by gas-liquid chromatography (GLC) for 4–5 h at one partial pressure, then the gas mixture was changed and bubbled through the solution for 5 min, and the new reaction rate determined. The rate of exidation of 2-propanol increased linearly with increasing dioxygen pressure

$$-d[ROH] dt = P_{ch} [r \pm 1]^{-1}$$
(3)

Dependence of the Rate of Reaction on the Concentration of 2-Propanol. The rate of oxidation of 2-propanol at the platinum catalyst/electrode was independent of its concentration. Zeroorder plots of the change in concentration of 2-propanol with time were obtained for the oxidation of 1.20 mmol of 2-propanol on a platinized platinum gauze electrode in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> (1.0 atm of O<sub>2</sub>). For one particular run, the initial concentration of 2-propanol decreased to 0.14 M (at t = 4.0 h), the concentration of 2-propanol was observed.

Dependence of Rate on the Surface Area of Catalyst. Because the surface area of the platinized catalyst/electrode used in most of these studies could not be conveniently altered, these studies were carried out using two different platinized platinum wires, the first having a geometric surface area of 9.96 cm<sup>2</sup> and a real surface area (measured by galvanostatic charging) of 1700 cm<sup>2</sup> and the second having a geometric surface area of 12.9 cm<sup>2</sup> and a real surface area of 3500 cm<sup>2</sup>. The reactions were run in a three-compartment electrochemical cell of standard design, using as nearly identical stirring rates as could be attained with the same stirring bar and magnetic stirrer. The physical configuration of the two platinum wires was approximately the same, both wrapped as wire coils with roughly the same dimensions. The rates of oxidation obtained by using the electrodes having surface areas of 1700 and 3500 cm<sup>2</sup> were 0.22  $\pm$  0.01 and 0.42  $\pm$  0.02  $\mu$ mol/min, respectively; that is, a 2-fold increase in the surface area of the electrode resulted in a 2-fold increase in the rate of reaction and indicated a first-order dependence of the reaction on the surface area of the platinum catalyst. A similar result has

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<sup>(18)</sup> Adams, R. N. *Electrochemistry at Solid Electrodes*; Dekker: New York, 1969; Chapter 4.



**Figure 2.** Ratio of acetone- $d_0$  to acetone- $d_6$  (O, first run;  $\Box$ , second run) and percent reaction ( $\bullet$ , first run;  $\blacksquare$ , second run) during the course of an oxidation of an equimolar solution of 2-propanol- $d_0$  and 2-propanol- $d_7$ .

been reported for this same reaction using a 1% Pt/C catalyst.<sup>19</sup> The rate equation for the reaction on platinum metal under these reaction conditions is then

$$-d[ROH]/dt = k(\omega^{0.6})[ROH]^0[Pt_s]^1 P_{O_s}^{-1}$$
(4)

Deuterium Isotope Effect. A comparison of the rate of oxidation of 2-propanol- $d_0$  and 2-propanol- $d_7$  in 0.20 N H<sub>2</sub>SO<sub>4</sub> established that no rate-limiting carbon-hydrogen bond formation or cleavage occurred during oxidation to acetone; a  $k_{\rm H}/k_{\rm D}$  of 1.03  $\pm$  0.04 was obtained. This result is that expected for a reaction that is mass-transport limited in dioxygen. For determination of whether a non-rate-limiting deuterium isotope effect could be observed, a competitive  $k_{\rm H}/k_{\rm D}$  was measured by performing an oxidation with equal amounts of 2-propanol- $d_0$  and 2-propanol- $d_7$ present in the solution and monitoring the ratio of acetone- $d_0$  to acetone- $d_6$  produced by GC/MS. The reaction rate determined for the oxidation with both 2-propanol- $d_0$  and 2-propanol- $d_7$ present was the same as observed for 2-propanol- $d_0$  alone. Figure 2 illustrates the ratio of acetone- $d_0$  to acetone- $d_6$  over the course of the reaction for two separate runs; the agreement between the two runs was excellent, and a competitive  $k_{\rm H}/k_{\rm D}$  of 3.3 ± 0.3 was observed during the first 40% of the reaction. After the reaction reached 40% completion, where the solution was 0.038 M in 2-propanol- $d_0$  and 0.082 M in 2-propanol- $d_8$ , the ratio of acetone- $d_0$ /acetone- $d_6$  slowly decreased until at the completion of the reaction it was ca. 1:1. A number of GC/MS analyses of an authentic 1:1 mixture of acetone- $d_0$  to acetone- $d_6$  indicated that the mixture was 0.96/1.00 acetone- $d_0$ /acetone- $d_6$ , yielding an experimental error of  $\pm 5\%$  for this method.

Reversibility of the Dehydrogenation Step. We carried out an oxidation of 2-propanol (0.20 M) in the presence of 2-butanone (0.20 M) and monitored the reaction mixture by GLC throughout the course of the reaction to determine whether any 2-butanol was produced. The reaction rate in the presence of 0.20 M 2-butanone was  $1.02 \pm 0.04 \,\mu$ mol/min, ca. 40% slower than the reaction rate measured in the absence of added 2-butanone. The formation of 2-butanol was not observed (<0.5% by GLC) at any time during the reaction. The oxidation of 2-butanol (0.20 M) was also performed in the presence of added acetone (0.20 M), and no 2-propanol (<0.5% by GLC) was detected during the course of the reaction. The rate of reaction for oxidation of 2-butanol in the presence of 0.20 M acetone was  $1.17 \pm 0.03 \,\mu$ mol/min and was comparable to the rate of oxidation of 2propanol in the presence of 2-butanone.

Oxidation of 2-Propanol Using Hydrogen Peroxide in Place of Dioxygen. Hydrogen peroxide spontaneously decomposes to dioxygen and water when it comes in contact with platinum metal (eq 5).<sup>20</sup> Because the rate of oxidation of 2-propanol is first order

$$2H_2O_2 \xrightarrow{P_1} O_2 + 2H_2O \tag{5}$$



Figure 3. Production of acetone ( $\bullet$ ) and open-circuit potential ( $\blacksquare$ ) of the catalyst during the oxidation of 1.20 mmol of 2-propanol in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> on a platinized platinum gauze electrode by addition of 20-µL (0.15 mmol) aliquots of 30% H<sub>2</sub>O<sub>2</sub> under argon.

in the partial pressure of dioxygen and mass transport of dioxygen to the catalyst/electrode surface is the overall rate-limiting step, the generation of dioxygen in high concentration at the catalyst surface was studied in an attempt to change the rate-limiting step of the reaction.

Under an argon atmosphere, 1.20 mmol of 2-propanol was added to 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> in the working electrode compartment of the electrochemical cell containing the standard catalyst/electrode. While the catalyst/electrode was stirred at 900 rpm, a 20- $\mu$ L aliquot (0.15 mmol) of 30<sup>%</sup> H<sub>2</sub>O<sub>2</sub> was added to the cell. Dioxygen was formed at the catalyst surface. The yield of acetone upon complete reaction of the  $H_2O_2$  (after ca. 10 min) was 0.13 mmol (86% based on added  $H_2O_2$ ). The addition of 20- $\mu$ L aliquots of 30% H<sub>2</sub>O<sub>2</sub> was continued, and the progress of the reaction followed by GLC (Figure 3). The sixth aliquot of 30% H<sub>2</sub>O<sub>2</sub> that was added was 150  $\mu$ L (1.13 mmol); dioxygen was evolved vigorously at the catalyst surface, but the yield of acetone produced was only 0.10 mmol (9% based on added  $H_2O_2$ ). It appears that 2-propanol competes poorly with a comparable concentration of H<sub>2</sub>O<sub>2</sub> for catalytic sites on the platinum catalyst/electrode surface.

A constant slow addition of hydrogen peroxide to a solution of 1.2 mmol of 2-propanol- $d_0$  in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> was performed at a rate of ca. 8.0  $\mu$ L (0.060 mmol) 30% H<sub>2</sub>O<sub>2</sub>/min using a syringe pump, to keep the concentration of H<sub>2</sub>O<sub>2</sub> small relative to that of 2-propanol. During the first 6 min of the reaction no dioxygen evolved, and the rate of addition of H<sub>2</sub>O<sub>2</sub> exactly equalled the rate of production of acetone. After 6 min of reaction, the rate of oxidation slowed to 20% of the rate of addition of H<sub>2</sub>O<sub>2</sub>, and dioxygen evolution was observed at the catalyst surface (Figure 4). The reaction was repeated using 1.12 mmol of 2-propanol- $d_7$ , and almost identical results were obtained; the rate of oxidation in the first 6 min was the same as for 2propanol- $d_0$  ( $k_{\rm H}/k_{\rm D} = 1.0$ ), and for the remainder of the reaction  $k_{\rm H}/k_{\rm D} = 1.2 \pm 0.2$ .

A comparison of the rates of reaction for both 2-propanol- $d_0$ and  $-d_7$ , obtained by using dioxygen at 1 atm with the rates obtained by using slow addition of 30% H<sub>2</sub>O<sub>2</sub> indicated that when H<sub>2</sub>O<sub>2</sub> is used, the oxidation initially proceeded at a rate (60)

<sup>(19)</sup> Nicoletti, J. W.; Whitesides, G. M. J. Phys. Chem., preceding paper in this issue.

<sup>(20)</sup> Hoare, J. P. The Electrochemistry of Oxygen; Wiley: New York, 1968; Chapter 2.



**Figure 4.** Relative rates of production of  $acetone-d_0$  ( $\bullet$ ) and  $acetone-d_6$  ( $\blacksquare$ ) from the oxidation of 2-propanol- $d_0$  and 2-propanol- $d_7$  (0.20 M), respectively, by oxidation with hydrogen peroxide at a constant addition rate of 60  $\mu$ mol/min.

 $\mu$ mol/min) ca. 60 times faster than the rate observed when dioxygen (1 atm) was used as the oxidant. After a short interval (ca. 6 min, PROD<sub>s</sub> = 3-4), the initial reaction rate decreased to a steady-state rate ca. 10 times faster than that observed by using dioxygen at 1 atm; no further decrease in activity or poisoning of the catalyst was observed. Hydrogen peroxide thus appears to be an effective oxidant for the catalytic oxidation of 2-propanol on platinum.

Open-Circuit Catalyst/Electrode Potential during Oxidation of 2-Propanol Using Dioxygen. We used the open-circuit potential of the catalyst/electrode to infer the species present on the platinum surface while the catalytic reaction was occurring. The reference electrode was a Ag/AgCl (saturated), Na<sub>2</sub>SO<sub>4</sub> (1.0 M)/Na<sub>2</sub>SO<sub>4</sub> (1.0 M) double-junction (dj) system.<sup>21</sup> Open-circuit potentials measured against this (Ag/AgCl dj) reference electrode are shifted -0.370 V with respect to potentials measured versus a standard hydrogen electrode (SHE).

Dihydrogen is produced on a platinum electrode in 0.20 N  $H_2SO_4$  at -0.460 V (Ag/AgCl dj), and coverage of the electrode surface with adsorbed hydrogen steadily decreases from that of a monolayer as the potential is increased from -0.460 to -0.050V (Ag/AgCl dj). In the potential range between -0.050 and +0.400 V (Ag/AgCl dj), the platinum surface is occupied by neither adsorbed hydrogen nor oxygen; proceeding from +0.400 to ca.  $\pm 1.100$  V, the surface becomes increasingly oxidized by the formation of platinum oxide. Dioxygen evolution begins at potentials more positive than ca. +1.100 V. Observation of an open-circuit potential for the electrode/catalyst, in the range of -0.050 to -0.460 V (Ag/AgCl dj) indicates that hydrogen is present on the surface of the platinum catalyst; catalyst potentials more positive than +0.400 V indicate oxidation of the catalyst surface, probably by the formation of platinum oxide. We note explicitly that the observed open-cell potentials are not entirely straightforward to interpret for the complex electrode geometry used in these experiments. Local differences in surface potential and in the composition of the platinum-water interface may be possible due to contributions to local cell potential from resistive and capacitative terms and perhaps to differences in local solution concentrations of reactants, products, and protons. We believe that the observed open-cell potentials reflect a qualitative but accurate image of the average catalyst/electrode surface

The open-circuit potential of the platinized platinum gauze electrode during the course of the oxidation of 2-propanol with dioxygen is shown in Figure 5. Before 2-propanol was added to the working electrode compartment containing  $0.20 \text{ N H}_2\text{SO}_4$ under 1.0 atm of O<sub>2</sub>, the potential of the platinum electrode was ca. +0.520 V (Ag/AgCl dj). This initial electrode potential indicated that partial oxidation of the electrode surface had taken



**Figure 5.** Production of acetone ( $\bullet$ , r = 1.14 mmol/min;  $\blacksquare$ ,  $r = 1.13 \mu \text{mol/min}$ ) and open-circuit catalyst potential ( $\bigcirc$ ,  $\square$ ) for two consecutive oxidations of 1.20 mmol of 2-propanol by oxygen (1.0 atm) in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> (stirring rate = 440 rpm, Ag/AgCl dj reference electrode).

place by reaction with dioxygen to form platinum oxides. Addition of 2-propanol to the solution with stirring resulted in an immediate, rapid drop in the electrode potential to -0.276 V, indicating that the reaction of 2-propanol at the surface of the electrode reduced the platinum oxide and produced a surface partially covered with adsorbed hydrogen.

The potential of the electrode remained in the range of -0.275 to -0.050 V (Ag/AgCl dj) until the concentration of 2-propanol had decreased from 0.20 to 0.01 M (~95% reaction). The potential gradually increased to ca. +0.30 V during the completion of the last 5% of the reaction. Removing the reaction mixture from the working electrode compartment, rinsing the catalyst/ electrode, and repeating the reaction under the same conditions produced potential-time curves indistinguishable from the first (Figure 5).

The most important conclusion from these data is that the catalyst/electrode surface was partially covered with adsorbed hydrogen during the major part of the oxidation of 2-propanol. It was not until the concentration of 2-propanol decreased from 200 to 10 mM that dioxygen (ca. 1.3 mM at equilibrium under reaction conditions)<sup>22</sup> apparently was able to compete successfully with 2-propanol for the catalyst active sites. This result implies that the oxidation proceeds by reaction of 2-propanol with a platinum surface that is in a predominantly reduced state and not with a surface that is covered with adsorbed oxygen or is otherwise oxidized.

The dependence of the open-circuit potential of the platinum catalyst on the concentration of 2-propanol, acetone, and dioxygen was checked by changing the concentration of each individually, under the conditions used in the reaction, while holding all other parameters constant. Changing the concentration of 2-propanol or the pressure of dioxygen resulted in much larger changes in the catalyst potential than those resulting from changes in the concentration of acetone (Figure 6). This result demonstrates that the catalyst/electrode potential was determined primarily by the relative concentration of 2-propanol and dioxygen in solution. Although acetone is known to adsorb on a clean platinum surface,<sup>23,24</sup> it apparently does not compete well with dioxygen

<sup>(21)</sup> A saturated calomel reference electrode (SCE) was initially used as the reference electrode, but chloride ion from the electrolyte of the SCE was found to poison the reaction.

<sup>(22)</sup> Linke, W. F. Solubilities of Inorganic and Metal Organic Compounds; D. Van Nostrand: New York, 1965; Vol. 2, p 1229.



**Figure 6.** Open-circuit catalyst potential dependence on the concentration of acetone ( $\bullet$ ) and 2-propanol ( $\blacksquare$ ), and on the partial pressure of dioxygen ( $\blacktriangle$ ) during a catalytic oxidation of 2-propanol to acetone with dioxygen on a platinized platinum gauze electrode.

or 2-propanol; this inference is corroborated by the observation that the rate of the catalytic oxidation reaction did not decrease as the acetone concentration increased over the course of the reaction.

Catalyst Potential during Open-Circuit Oxidations Using Hydrogen Peroxide. Prior to the addition of hydrogen peroxide, the open-circuit potential of a platinized platinum gauze electrode in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> that was also 0.20 M in 2-propanol under 1 atm of argon was ca. -0.315 V (Ag/AgCl dj). This potential is 45 mV more negative than the lowest potential recorded for oxidation under 1 atm of dioxygen, an observation that indicates that the stripping of oxide from the platinum surface by the dehydrogenation of 2-propanol was never complete when the reaction was run under 1 atm of dioxygen. In neither reaction did the potential of the electrode reach -0.460 V (Ag/AgCl dj). the value corresponding to a platinum surface covered with a monolayer of adsorbed hydrogen (1H/1Pt<sub>s</sub> atom).

When 20  $\mu$ L (0.15 mmol) of 30% H<sub>2</sub>O<sub>2</sub> was added with stirring to the compartment containing the catalyst/electrode (1.20 mmol of 2-propanol in 6 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> under argon), the potential of the catalyst immediately increased from -0.315 to +0.417 V (Ag/AgCl dj) and evolution of some dioxygen was observed. After ca. 3 min, the potential of the catalyst at first rapidly and then more slowly decreased to -0.294 V (Figure 3). During the process, 0.13 mmol of acetone was generated (86% yield based on added  $H_2O_2$ ). Continued addition of 20-µL aliquots of hydrogen peroxide produced results indistinguishable from that observed for the first aliquot. When the reaction was run by using a slow constant addition of 8  $\mu$ L (0.060 mmol) of 30% H<sub>2</sub>O<sub>2</sub>/min rather than the addition of aliquots, the open-circuit potential of the platinized platinum gauze electrode quickly increased from -0.315 V (Ag/AgCl dj) at the start of the reaction to +0.420 V during the first 2 min and remained at this potential throughout the reaction. No poisoning of the catalyst was observed when hydrogen peroxide was used as the oxidizing agent.

### Discussion

The cathodic displacement of open-circuit potential of a platinum catalyst during the oxidation of alcohols by dioxygen has been interpreted previously to indicate that the surface of the catalyst was partially covered with adsorbed hydrogen.<sup>10,12,25</sup> We concur with this conclusion. Our observations established further that addition of 2-propanol to the working electrode compartment containing a partially oxidized platinized platinum gauze electrode resulted in an immediate cathodic displacement of the catalyst

SCHEME I: Proposed Mechanism for the Oxidation of 2-Propanol on Platinum with H<sub>2</sub>O<sub>2</sub>



potential to a potential indicative of a surface predominantly covered with adsorbed hydrogen. Similar results have been reported for the open-circuit reduction of electrochemically produced platinum oxide in aqueous solution by reaction with alcohols,<sup>26</sup> formic acid,<sup>27–29</sup> and dihydrogen.<sup>30–32</sup> The open-circuit reduction of platinum oxide layers by hydrogen in aqueous solution is believed to occur by an electrochemical local-cell mechanism: dihydrogen dissociates on one part of the catalyst surface, and reduction of platinum oxide may occur at a second part that is physically separated (although electrochemically connected). Islands of oxide-free platinum are thought to be produced as the reduction occurs. Direct chemical reaction between surface platinum oxide and dihydrogen may also occur<sup>33</sup> but is believed to be a minor pathway.

Reaction of formic acid also reduces chemisorbed oxygen on a platinum surface by a local cell mechanism.<sup>27–29</sup> The reduction of platinum oxide by alcohols is believed to proceed by a mechanism similar to that proposed for reduction by dihydrogen.<sup>34</sup> Again, a direct chemical reaction may make some contribution to the overall reaction.

The open-circuit potential of the platinized platinum gauze electrode reaches an equilibrium value of ca. -0.330 V (Ag/AgCl dj) with stirring in a 0.20 N H<sub>2</sub>SO<sub>4</sub> solution also 0.20 M in 2-propanol under 1 atm of argon, indicating significant coverage of the electrode surface with hydrogen but not the formation of the complete monolayer that would be indicated by an open-circuit potential of ca. -0.460 V (Ag/AgCl dj). This result may imply that not every surface platinum atom is a suitable site for the dehydrogenation of 2-propanol to acetone. The open-circuit potential of the catalyst under 1 atm of dioxygen remains in the potential range of -0.275 to -0.050 V (Ag/AgCl dj) for almost the entire reaction, indicating that the surface remains covered with hydrogen and mass transport of oxygen to the catalyst surface is rate limiting. This electrochemical inference is supported by the observed kinetics.

Platinum-catalyzed oxidation of 2-propanol by hydrogen peroxide was explored in an effort to circumvent the mass-transport limited delivery of dioxygen to the catalyst surface. Under open-circuit conditions, such as those used in this study, the catalytic decomposition of  $H_2O_2$  on platinum is believed to proceed via an electrochemical local cell (mixed potential) mechanism in

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#### Oxidation of 2-Propanol to Acetone

which adsorbed oxygen layers or surface oxides are present.<sup>35–37</sup> A surface platinum oxide may be an intermediate in this reaction. Bianchi et al.<sup>38</sup> have proposed a chemical pathway for the decomposition of  $H_2O_2$  by reaction with surface platinum oxide.

When hydrogen peroxide was used as the oxidizing agent for the oxidation of 2-propanol to acetone, the open-circuit potential of the electrode during reaction was ca. 0.87 V (normal hydrogen electrode), a value that corresponds to the open-circuit potential observed for the decomposition of hydrogen peroxide on platinum metal in the absence of 2-propanol.<sup>38,39</sup> The surface of the catalyst was thus predominantly in an oxidized state, partially covered with platinum oxide when hydrogen peroxide was used as the oxidant, rather than being predominantly covered with surface hydrogen as it appears to be when dioxygen was used as the oxidant. Approximately 1 equiv of 2-propanol was oxidized for each equivalent of  $H_2O_2$  consumed for most of the reaction. Scheme I suggests a possible mechanism for the oxidation of 2-propanol by hydrogen peroxide.

The rate of oxidation of 2-propanol observed by using a constant slow addition of  $H_2O_2$  was initially 60 times faster than that observed under the same conditions using oxygen as oxidant. It is not clear, however, that the reaction was no longer masstransport limited: the instantaneous concentration of  $H_2O_2$  in the solution was probably very small (<10<sup>-4</sup> M) since the rate of production of acetone was initially equal to the rate of addition of  $H_2O_2$ , and no difference in the rate of oxidation of 2-propanol- $d_0$ and  $-d_8$  was observed. Although the reaction ran more rapidly using hydrogen peroxide rather than dioxygen as an oxidant, the transport of hydrogen peroxide or 2-propanol to the surface of the catalyst may still have been rate limiting.

Catalyst Deactivation. One explanation that has been proposed for catalyst deactivation during the oxidation of alcohols involves irreversible or slowly reversible reactions of dioxygen with the platinum surface. Adsorption of catalyst poisons and/or reaction products have also been involved. Catalyst deactivation during the oxidation of 2,3-4,6-diacetone-L-sorbose on supported platinum catalysts was studied by Jaffe and Pleven,15 who found that the rate of catalyst deactivation was markedly reduced by controlling the dioxygen concentration at low partial pressures. For the oxidation of glucose<sup>14</sup> and ethylene glycol<sup>40</sup> when platinum on carbon catalyst in aqueous solution is used, catalyst deactivation could be partially reversed by temporarily stopping the addition of oxygen to the reaction: in this oxygen-deficient state, the oxidized (deactivated) catalyst was re-reduced to an active form by reaction with glucose or ethylene glycol. The deactivated catalyst could also be partially regenerated by treatment with an aq formaldehyde solution under nitrogen. Complete regeneration of catalyst activity for ethylene glycol oxidation was obtained by treating the deactivated catalyst with oxygen and then hydrogen at 300 °C.

These studies suggest that bare platinum(0) is more active as a catalyst than is platinum oxide and that alcohol oxidation should be considered primarily as a dehydrogenation catalyzed by platinum(0), followed by an oxidation step to regenerate Pt(0)from surface platinum hydride. In the systems studied here, no catalyst deactivation was observed after ca. 500 h of consecutive





<sup>a</sup>The interaction of dioxygen and oxygen with the platinum is entirely schematic.

oxidations (PROD<sub>s</sub> = 400) under oxygen-starvation conditions. This resistance to poisoning may not, however, be representative: the rate of oxidation over this catalyst is very slow compared to reaction rates obtained under similar conditions with highly dispersed supported catalysts. The absence of catalyst deactivation due to reaction of dioxygen with the platinized platinum electrode used in this study is consistent with reports relating the degree of catalyst deactivation by reaction with dioxygen to catalyst dispersion, where increasing catalyst deactivation is observed with increasing dispersion.<sup>19,41-43</sup>

Mechanism of the Platinum-Catalyzed Oxidation of 2-Propanol. The mechanism of reaction that is most compatible with the experimental results described in this paper (obtained under open-circuit and O<sub>2</sub> mass-transport-limited conditions using the platinized platinum gauze catalyst/electrode), as well as with previously reported information regarding the adsorption and oxidation of alcohols, is outlined in Scheme II. The open-circuit potential of the electrode under active catalytic conditions indicates that the surface of the catalyst is predominantly but not completely covered with adsorbed hydrogen, even though the reaction is run under 1 atm of oxygen. The first step of the reaction involves chemisorption of 2-propanol at the catalyst surface. This reaction might occur by insertion of a platinum atom into either the O–H bond or the  $\alpha$ -C–H bond of 2-propanol. Although we cannot distinguish between these alternatives, the former is more likely.

Although addition of the  $\alpha$ -C-H bond of aliphatic alcohols to platinum surfaces has often been claimed in studies of the adsorption and electrochemical oxidation of alcohols on platinum electrodes,<sup>44-47</sup> little evidence supports these claims. In contrast, numerous studies of the reactions of alcohols at platinum<sup>48</sup> and

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other transition-metal surfaces<sup>49-54</sup> have presented evidence for the formation of surface alkoxides by insertion into the O–H bond. A variety of homogeneous platinum(0) complexes have also been observed to form stable platinum methoxide complexes by reaction with methanol.<sup>55,56</sup>

After adsorption of 2-propanol on the catalyst surface, the chemisorbed species (presumably a surface alkoxide) dehydrogenates by  $\beta$ -hydride elimination of a hydrogen atom to the surface of the catalyst to form acetone (Scheme II). Competitive oxidation of an equimolar mixture of 2-propanol- $d_0$  and 2-propanol- $d_7$  established an isotope effect of  $k_{\rm H}/k_{\rm D}$  of  $3.2 \pm 0.3$  for the transfer of hydrogen (deuterium) to the catalyst surface. A similar competition experiment using 2-propanol-2- $d_1$  and 2-propanol with Adam's catalyst (platinum black) gave  $k_{\rm H}/k_{\rm D}$  of  $1.9 \pm 0.4$ .<sup>57</sup> A kinetic deuterium isotope effect of 1.7 has been reported for the decomposition of CH<sub>3</sub>OH and CD<sub>3</sub>OH on platinum, a reaction in which the rate-limiting step is believed to be the cleavage of a C-H bond of an intermediate surface alkoxide.<sup>58,59</sup>

Dehydrogenation was irreversible; oxidation of 2-propanol in the presence of 2-butanone produced no (<0.5%) 2-butanol (via trans-hydrogenation); the analogous result was obtained when 2-butanol was oxidized to 2-butanone in the presence of acetone. The irreversibility of alcohol dehydrogenation on platinum has been demonstrated previously by oxidizing ethanol or 2-propanol with dioxygen on platinum catalysts in H<sub>2</sub><sup>18</sup>O and observing no incorporation of <sup>18</sup>O into the remaining alcohol.<sup>11</sup>

The hydrogen remaining on the platinum catalyst surface after the dehydrogenation of 2-propanol to acetone is oxidized to protons (or water) by reaction with an oxidizing species derived from dioxygen. It is not clear whether the active oxidant is a surface platinum oxide, chemi- or physiadsorbed hydrogen peroxide, or dioxygen under the reaction condition used in catalysis. Independent experiments establish that platinum surface oxides are rapidly reduced by 2-propanol and that hydrogen peroxide is an effective oxidant toward 2-propanol in the presence of platinum. An electrochemical local cell mechanism<sup>60,61</sup> (i.e., a reaction involving oxidation of Pt-H to Pt(0) and H<sup>+</sup> and reduction of some oxygen containing species to H<sub>2</sub>O at separate sites on the surface, without direct transfer of H to PtO or PtO<sub>2</sub>) may be operative in the important processes.

Implications for Synthesis. We suggest that the platinumcatalyzed oxidation of alcohols by dioxygen to ketones be considered a coupled, two-reaction system. One reaction is the platinum(0)-catalyzed *dehydrogenation* of alcohol to ketone; the second is the platinum-catalyzed oxidation of platinum surface hydride to water by dioxygen. The high selectivity of the system

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is well established and highly useful, especially for carbohydrates and related water-soluble substances. Its major practical drawbacks are relatively slow catalytic rates (with an attendant requirement for large quantities of catalyst) and relatively rapid catalyst deactivation (also requiring large quantities of catalyst). Major questions in synthesis are thus how can the rate be increased? How can catalyst deactivation be slowed?

It is clear that, with the experimental system employed here, mass transport of dioxygen from the vapor phase to the catalyst surface limits the overall rate of reaction. Thus, to increase the rate, it would be necessary to increase the rate of delivery of oxidizing equivalents to the catalyst surface. Increasing the pressure of dioxygen provides one approach to this problem; using hydrogen peroxide seems to provide a second. We believe that substitution of hydrogen peroxide for dioxygen in this reaction may provide an attractive method of carrying out rapid reoxidation without the practical problems of handling and dispersing dioxygen under pressure or with vigorous agitation.

The form of the bulk platinized catalyst used in this work was dictated by the experimental requirement for both catalytic activity and electrochemical tractability. This catalyst proved resistant to poisoning and thus provided little information about mechanisms of poisoning. It is also, of course, not a practical catalyst system because it has a low dispersion and hence inefficient use of platinum. In related studies<sup>19</sup> we have examined highly dispersed, supported catalysts and established that the rate of deactivation of the catalyst correlated with its dispersion. One interpretation of this result is that small, highly active catalyst particles are subject to relatively rapid oxidative conversion to a catalytically inactive platinum oxide. The practical motivation in synthesis to use highly dispersed catalysts to achieve efficient use of platinum thus appears to be at odds with the advantage in catalyst lifetime achieved with low dispersion catalysts. High pressures of dioxygen (and perhaps use of hydrogen peroxide) also seem to hasten the overoxidation of small catalyst particles to an inactive form. The best catalyst for use in synthesis will thus be one with a sufficiently high dispersion to be economical in its use of platinum and a sufficiently low dispersion (and concentration of dioxygen and/or hydrogen peroxide) to give long catalyst lifetimes.

From the results obtained by using hydrogen peroxide in place of oxygen in the catalytic oxidation of 2-propanol reported here, it is possible that highly selective oxidations of alcohols on supported platinum catalysts of high dispersion with little or no catalyst deactivation might be attained by using hydrogen peroxide as the oxidant, if  $H_2O_2$  could be added at a rate sufficient to produce reasonable rates of oxidation without irreversibly oxidizing the surface of the platinum catalysts as is believed to occur with dioxygen.

### **Experimental Section**

General Methods. Water used in all reactions was pretreated by passing distilled water through a Barnstead ion-exchange column, distilling through a Corning AG-1b distillation apparatus, and shaking with  $\gamma$ -alumina (Strem). Ultrahigh-purity (UHP) H<sub>2</sub>SO<sub>4</sub> (Alfa), 2-propanol (Baker, HPLC grade), 2-butanone (Baker, HPLC grade), 2-butanol (Aldrich, reagent grade), 30%  $H_2O_2$  (Baker), and 2-propanol- $d_8$  (Aldrich) were all used as received. Argon (Matheson, UHP, 99.999%, deoxygenated by Oxisorb) and dioxygen (Matheson, UHP, 99.999%) were saturated with water by passing through gas-washing bottles containing distilled water prior to use. Cyclic voltammetry was carried out with a Princeton Applied Research Model 175 universal programmer and Model 174A polarographic analyzer, and galvanostatic charging and controlled potentiometry were performed by using a Princeton Applied Research Model 371 potentiostat-galvanostat. Current-potential curves, potential-time curves, and galvanostatic charging curves were recorded on a Nicolet Explorer I oscilloscope and an Omnigraphic 2000 X-Y recorder. Mass spectra were obtained on a Hewlett-Packard 5990A GC/MS by using an ionization potential of 70 eV.

Open-Circuit Oxidation of 2-Propanol by Dioxygen on a Platinized Platinum Gauze Electrode. Before placing the working

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electrode in the cell, it was pretreated by soaking in concentrated HNO<sub>3</sub> for 2 h, rinsed thoroughly with doubly distilled, deionized water, then placed in 50 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub>, and held at a constant potential of +1.200 V (Ag/AgCl single-junction reference electrode) until the open-circuit potential was +1.000 V, then at -0.320 V until the open-circuit potential was -0.300 V. The electrode was then placed in the working electrode compartment of the electrochemical cell, and 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> added. With a Teflon needle,  $O_2$  was bubbled into the electrolyte for 5 min, and the cell placed under a static head of oxygen. The working electrode was stirred at a constant rate by using a Fisher Dynamix overhead stirrer, and the stirring rate monitored with a strobe light. To the working electrode compartment was then added 92.0 µL (72.2 mg, 1.20 mmol) of 2-propanol (Baker HPLC) by microliter syringe with stirring. The potential of the working electrode was monitored with both a Nicolet Explorer I digital oscilloscope and a Beckman 3010 digital multimeter.

With a 10- $\mu$ L syringe, 1.0- $\mu$ L aliquots of the solution in the working electrode compartment were withdrawn through the sample port at predetermined intervals and analyzed by GLC on a 3% Carbowax 20 M on Chromosorb W column. No internal standard was used; the progress of the reaction was determined from the relative ratio of 2-propanol to acetone. Mass balance remained constant throughout the reaction. At the completion of the reaction, the solution was withdrawn by syringe with a Teflon needle, and 6.0 mL of fresh 0.20 N  $H_2SO_4$  added to the working compartment. The electrode was stirred in this solution for 5 min, then the solution was withdrawn and replaced with 6.0 mL of fresh 0.20 N  $H_2SO_4$  and the rinse cycle repeated. The second wash was removed and replaced with 6.0 mL of 0.20  $H_2SO_4$ , and  $O_2$  was bubbled through the solution for 5 min before another 92-µL aliquot of 2-propanol was added to the cell for oxidation.

Dependence of the Open-Circuit Potential of a Platinized Platinum Gauze Electrode on the Concentration of 2-Propanol, Acetone, and Oxygen. The potential dependence on isopropyl alcohol concentration was determined by allowing the oxidation of 1.20 mmol of 2-propanol in 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub> (1 atm O<sub>2</sub>, 900 rpm) to proceed to 20% completion, and then the concentration of 2-propanol at this point (0.16 M) was increased by consecutive additions of 0.30-mmol aliquots of 2-propanol while monitoring the open-circuit potential: 0.16 M 2-propanol, -0.189 V (Ag/AgCl dj); 0.21 M, -0.200 V; 0.26 M, -0.208 V; 0.31 M, -0.213 V; 0.36 M, -0.217 V. The potential dependence on acetone concentration was determined after 20% reaction by consecutive additions of 0.30 mmol of acetone while monitoring the opencircuit potential: 0.04 M acetone, -0.200 V (Ag/AgCl dj); 0.06 M, -0.197 V; 0.14 M, -0.195 V; 0.19 M, -0.193 V. The potential dependence on the partial pressure of dioxygen was checked between 10% and 25% reaction at 0.23, 0.46, 0.75, and 1.0 atm O<sub>2</sub>, which yielded open-circuit potentials of -0.228, -0.200, -0.178, and -0.149 V, respectively.

Oxidation of 2-Propanol with Hydrogen Peroxide. To the working electrode compartment of the electrochemical cell was added 6.0 mL of 0.20 N H<sub>2</sub>SO<sub>4</sub>, and then argon was bubbled through the solution with a Teflon needle. The solution was placed under a static head of argon, and 92.0  $\mu$ L (1.20 mmol) of 2propanol was added while the working electrode was stirred at 900 rpm. The potential of the working electrode dropped to -0.315 V (Ag/AgCl dj), and from a check of the solution by GLC, the oxidation had proceeded to 4.5% completion by reaction of the 2-propanol with the partially oxidized electrode. To the working electrode compartment was then added 20  $\mu$ L (0.15 mmol) of 30%

 $H_2O_2$  with a 20-µL Gilsen autopipet (Model P20) under argon. Dioxygen evolution was observed at the platinum electrode, and the open-circuit potential rapidly rose to +0.417 V. After 3 min, the yield of acetone was 15.4% and the potential of the electrode began to decrease. After 25 min, the yield of acetone remained unchanged at 16.9% and the potential of the electrode was -0.294 V, indicating that the first aliquot had completely reacted and the surface of the electrode was once again covered with adsorbed hydrogen. A second 20- $\mu$ L aliquot of 30% H<sub>2</sub>O<sub>2</sub> was added, and after 3 min, the potential had once again risen to +0.420 V and the yield of acetone had increased to 27.7%. The potential then decreased to -0.287 V as the second aliquot of 30% H<sub>2</sub>O<sub>2</sub> was completely reacted. This cycle of addition of 30% H<sub>2</sub>O<sub>2</sub> was continued until the reaction had gone to 53.0% completion, at which point 150  $\mu L$  (1.13 mmol) of 30%  $H_2O_2$  had been added. Vigorous evolution of dioxygen was observed, but the yield of acetone increased only to 61.6% at 5 min after the addition.

A constant slow addition of 30% hydrogen peroxide was investigated instead of addition of 20-µL aliquots. The cell was prepared as described above, except that 7.5  $\mu$ L of 0.20 N H<sub>2</sub>SO<sub>4</sub> and 115  $\mu$ L (1.5 mmol) of 2-propanol were used. The 30% H<sub>2</sub>O was added with a syringe pump (Sage Instruments, Model 355). A 1.0-mL disposable tuberculin syringe was connected to a 2-ft length of 0.05-in. i.d.  $\times$  0.09-in. o.d. Tygon microbore tubing (VWR Scientific), and the other end of the tubing was attached to a 1-5-µL glass disposable micropipet (Curtin Matheson), which entered the cell through the rubber septum covering the sample port and was submerged below the surface of the solution. The tuberculin syringe was filled with the peroxide solution, which was added to the cell at ca. 8.0  $\mu$ L of 30% H<sub>2</sub>O<sub>2</sub> (0.060 mmol)/min. For the oxidation of 0.115 mL (1.50 mmol) of 2-propanol- $d_0$  in 7.5 mL of 0.20 N  $H_2SO_4$ , an initially rapid rate of oxidation was observed for the first 6 min of reaction, where the potential of the electrode increased from -0.315 to +0.412 V and the reaction ran to 35% completion (ca. 80 µmol/min for the first 6 min of reaction). The reaction rate then slowed to  $12.3 \pm 0.08 \ \mu mol/min$ for the remainder of the reaction and the reaction was discontinued after 66% completion. The above reaction was repeated with 115  $\mu$ L (1.48 mmol) of 2-propanol- $d_8$ , with very similar results (Figure 4). The reaction ran at ca. 75  $\mu$ mol/min for the first 6 min and then slowed to  $10.1 \pm 1.4 \ \mu mol/min$  for the remainder of the reaction  $(k_{\rm H}/k_{\rm D} = 1.2 \pm 0.2).$ 

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Supplementary Material Available: Dependence of the rate of oxidation of 2-propanol using a platinized platinum electrode/catalyst on stirring rate and partial pressure of dioxygen; kinetic plots of the oxidation of 2-propanol- $d_0$  and 2-propanol- $d_7$ on a platinized platinum electrode/catalyst; experimental methods for construction of the electrochemical cell, platinum gauze working electrode preparation and characterization, stirring-rate dependence, dioxygen partial pressure dependence, oxidation of 2-propanol in the presence of 2-butanone, and measurement of deuterium isotope effects for the oxidation of 2-propanol- $d_0$  and 2-propanol- $d_7$  (11 pages). Ordering information is given on any current masthead page.