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Use of a Porous Electrode for *in Situ* Mass Spectrometric Determination of Volatile Electrode Reaction Products

Sir:

The interpretation of the origin of products isolated after a bulk electrolysis is frequently subject to the problems caused by chemical reactions occurring between electrode intermediates and other species present in solution. In such situations, it is ordinarily considered desirable to identify an electrode intermediate as soon as possible after its production at the electrode, *i.e.*, at the electrode surface. We have developed a combined electrochemical–mass spectrometric technique that allows *in situ* qualitative and quantitative analysis of volatile intermediates and products generated during an electrochemical reaction. Our method uses a porous electrode, one side of which contacts the solution being electrolyzed, while the other side contacts the mass spectrometer's high-vacuum system.

As will be reported in the near future,[1] we have used this electrode to identify the gaseous products NO and N_2O generated at different potentials during the reduction of NO_2^- in 0.1 *M* $HClO_4$. The surface concentrations of these species have been determined quantitatively (estimated error 5–10%). We have also used the porous electrode under open-circuit conditions as a porous catalytic surface, verifying the well-known, spontaneous decomposition of hydrazine into nitrogen and hydrogen peroxide into oxygen. To our knowledge, this is the first report of the use of a controlled-porosity surface to interface a mass spectrometer directly to the site of a reaction. We believe this technique will be extremely useful for studying heterogeneous reactions involving gaseous products and/or reactants.

The electrode design we have used in the above-mentioned studies is shown in Figure 1 and allows only gas to be transported into the mass spectrometer inlet system. The electrode was fabricated by rubbing finely divided platinum into the slightly wetted fine glass frit. An aqueous TFE–Teflon dispersion was gently sucked into the frit, dried and baked to fuse the Teflon, and the teflonization procedure repeated until no more liquid would pass through the frit when a 1-atm pressure differential existed across it. Further details are given elsewhere.[2]

The purpose of this communication is to report the results we have obtained with the model system, the electrochemical generation of oxygen from 0.1 *M* $HClO_4$. Oxygen was generated from the oxygen-free perchloric acid solution at the porous electrode using selected constant anodic currents.

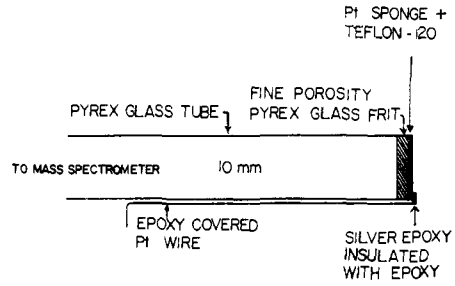

Figure 1. Schematic representation of porous electrode. Fritted end submerged in solution. Hitachi Perkin-Elmer RMU-6E instrument used.

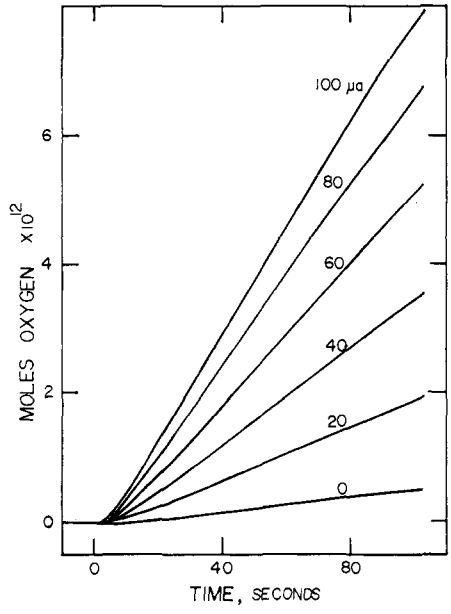

Figure 2. Mass-32 response *vs.* oxygen generation time.

The experiment shown in Figure 2 was performed by pumping out the vacuum system to 5×10^{-7} Torr, closing off the vacuum system from the pump, and recording the electron multiplier current at mass 32, using an *X*-time recorder, for the selected constant currents. The mass-32 response was calibrated in terms of moles of O_2 in the mass spectrometer by introducing a known quantity of oxygen.

The mass-32 response in Figure 2 rapidly becomes linear, and the slope of the linear portion is a measure of the rate of the electrochemical production of oxygen. The straight line portions do not pass through zero time, and there is evidence in Figure 2 for sorption effects within the vacuum system. These effects do not interfere in the interpretation of the linear portion of the response-time line.

Figure 3 is a plot of the limiting slope of the lines in Figure 2 *vs.* generation current. A straight line with a slope of 9.1×10^{-7} mol of O_2/C and a nonzero intercept corresponding to the leak rate of atmospheric oxygen into the mass spectrometer is obtained. The experimental slope indicates that 36% of the electrochemically generated oxygen enters the vacuum system of the mass spectrometer. Similar collection efficiencies have been obtained for hydrogen generated by constant-current reduction of 0.1 *M* $HClO_4$. These high collection efficiencies suggest that, in addition to gases, many or-

(1) S. Bruckenstein and R. Rao Gadde, paper in preparation.
(2) S. Bruckenstein and R. Rao Gadde, submitted for publication, *Anal. Chem.*

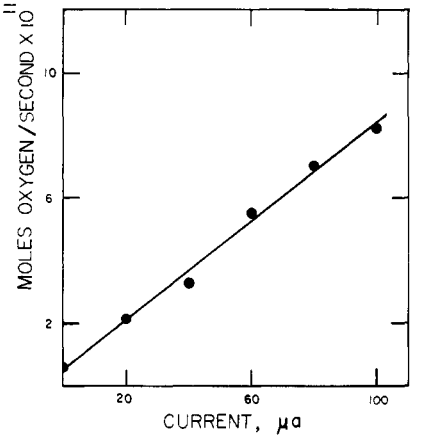

Figure 3. Oxygen flux to mass spectrometer as a function of generation current.

ganic species will have a sufficiently high volatility to be detected as they are produced during an electrochemical or a heterogeneous chemical reaction.

A detailed study of the properties of our porous electrode is given elsewhere.[2] The principal results of that study are as follows. (1) The collection efficiency of a volatile intermediate is only a weak function of the solution diffusion coefficient of the gas. (2) The electrode behaves as if about 50% of the available electrode surface exists below the visible electrode solution interface. (3) Gas transport through the electrode is principally by molecular, rather than viscous flow.

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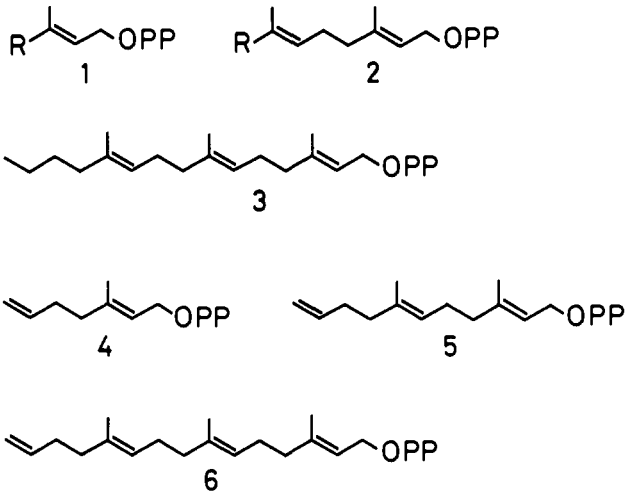
Formation of 16,16′-Bisnorgeranylgeranyl Pyrophosphate by Farnesyl Pyrophosphate Synthetase

Sir:

During the study of substrate specificity of farnesyl pyrophosphate synthetase of pumpkin, we found that the enzymic reaction of *trans*-3-methyl-2-heptenyl pyrophosphate (**1a**, R = *n*-C_4H_9) with isopentenyl pyrophosphate proceeded to the formation of a C_{18} compound, trishomofarnesyl pyrophosphate (**3**), *via* **2a** (R = *n*-C_4H_9), and that the reaction of the higher homologs (for example, **1b**, R = *n*-C_5H_{11} and **1c**, R = *n*-C_6H_{13}) stopped at the diprenyl homolog stage to give the corresponding derivatives of type **2**.[1] Popják, *et al.*, showed that the product derived from 6,7-dihydrogeranyl pyrophosphate by the liver enzyme was 10,11-dihydrofarnesyl pyrophosphate.[2] These findings suggested that the termination of the chain elongation by the prenyltransferase was determined by the size of the alkyl group of the product. However, it is not known whether this enzyme can afford a product possessing four double bonds of the tetraprenyl type. Therefore, we examined the effect of double bonds by comparison of C_8 compound **1a** and its dehydro derivative **4**, the former capable of reacting with isopentenyl pyrophosphate to afford the C_{18} compound **3** as well as the C_{13} compound **2a**. It was expected that the introduction of the $\Delta^{6,7}$ double bond into **1a** might cause "full stop" at the stage of a C_{13} compound, **5** (which is a farnesyl analog with respect to the double bonds), if the enzyme were "coded" by the number and position of the double bonds (see Chart I).

Chart I



-OPP = $-OP_2O_6^{3-}$

A mixture of methyl *cis*- and *trans*-3-methyl-2,6-heptadienoates, obtained by the Wittig reaction of 5-hexen-2-one with diethyl methoxycarbonylmethyl phosphonate, was hydrolyzed to the free acid, from which the trans isomer was isolated by recrystallization from petroleum ether (bp 50–60°). The trans structure was supported by the nmr spectrum in which a signal for the 3-methyl group appeared at δ 2.18 ppm in carbon tetrachloride.[1] The acid, mp 16–17°, was reduced with $LiAlH_4$ to *trans*-3-methyl-2,6-heptadienol,[3] which was then phosphorylated by a previously described method.[1] The pyrophosphate ester **4** was obtained as the lithium salt and characterized by the ir absorptions at 1120, 940, and 725 cm^{-1}.[4] Farnesyl pyrophosphate synthetase purified from pig liver according to the literature[5] was used for the present study, and the enzymic reaction of the artificial substrates with [^{14}C]isopentenyl pyrophosphate was examined in the usual way.[1] The incubation mixture contained, in a final volume of 2 ml, 40 μmol of phosphate buffer, pH 7.0, 10 μmol of $MgCl_2$, 0.1 μmol of [^{14}C]isopentenyl pyrophosphate (1.2 μCi/μmol), 0.05 μmol of **1a** or **4**, and *ca.* 50 μg of the enzyme. After the incubation at 37° for 1 hr, the mixture was treated with dilute acid to hydrolyze the allylic pyrophosphates. The amounts of [^{14}C]isopentenyl pyrophosphate converted into the acid-labile allylic pyrophosphates by the condensation with **1a** and **4** were 30,900 and 34,400 dpm, respectively. The control incubations of [^{14}C]isopentenyl pyrophosphate with and without geranyl pyrophosphate were carried out, and

(1) K. Ogura, T. Nishino, T. Koyama, and S. Seto, *J. Amer. Chem. Soc.*, 92, 6036 (1970).
(2) G. Popják, P. W. Holloway, and J. M. Baron, *Biochem. J.*, 111, 325 (1969).
(3) R. Helg, F. Zobrist, A. Lauchenauer, K. Brack, A. Caliezi, D. Stauffacher, E. Zweifel, and H. Schinz, *Helv. Chim. Acta*, 39, 1269 (1956).
(4) The absorption at 725 cm^{-1} can also be taken as a characteristic band for pyrophosphate esters (T. Nishino, unpublished results).
(5) P. W. Holloway and G. Popják, *Biochem. J.*, 104, 57 (1967).