These results strongly suggest that photolysis of acetylsilane in carbon tetrachloride involves a reaction in which chiral silyl radicals are formed, which show significant optical stability. Further studies to extend the scope of these reactions and to establish with greater certainty the existence of silyl radicals are in progress.

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(8) Holder of a National Research Council Postgraduate Scholarship, 1967–1969.

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Inhibition of the Reduction of Oxygen at a Platinum Electrode by the Deposition of a Monolayer of Copper at Underpotential

Sir:

The reduction of oxygen at platinum electrodes has been extensively studied, and it has long been recognized that appropriate pretreatment of the electrode is necessary to produce a mass transfer controlled current. Various hypotheses had been proposed for the decrease in the oxygen reduction current at an "activated" electrode surface. Among these are (1) changes in the surface structure of the activated electrode, *e.g.*, surface diffusion of platinum atoms;[1] (2) the slow reduction of surface oxides of platinum or chemisorbed oxygen which are responsible for the activation of the electrode and catalytically enhance the oxygen reduction process;[2] (3) inhibition and change in mechanisms of the reduction process by an adsorption of anions and/or cations;[3,4] and (4) adsorption of organic materials that inhibit the oxygen reduction process.[1] It seems unlikely that any one of these proposed processes can adequately explain all published results. The purpose of this communication is to present data which suggest that the deposition of metals at underpotential may be playing a major, and heretofore unsuspected, role in the time-dependent inhibition of the oxygen reduction process at platinum.

Deposition of copper on platinum at underpotentials has been studied using the rotating ring–disk electrode (rrde). Underpotential deposition of zerovalent copper (adatom adsorption) from $0.2\ M$ H_2SO_4 and $2 \times 10^{-5}\ M$ Cu(II) starts at potentials as positive as 0.5 V (*vs.* sce), and a complete monolayer will deposit at 0 V.[5] A potential of $\sim +0.6$ V is required to oxidize this monolayer from the platinum electrode. It has been reported that activation of a platinum electrode in sulfuric acid for oxygen reduction could be accomplished by anodizing the electrodes at $+1.15$ V for 1 min followed by reduction at -0.25 V for 60 sec.[1] We can activate the platinum disk of a rrde in $0.2\ M$ sulfuric acid containing trace Cu(II) by anodizing it at 0.6 V for 60 sec and then switching to a potential more negative than that required to reduce the platinum surface. Copper deposited at underpotential would be removed by this activation procedure. If silver, which produces a deactivation similar to copper, is present in solution, a potential of $+1.0$ V is necessary to remove silver deposited at underpotential and restore the activity of the electrode.

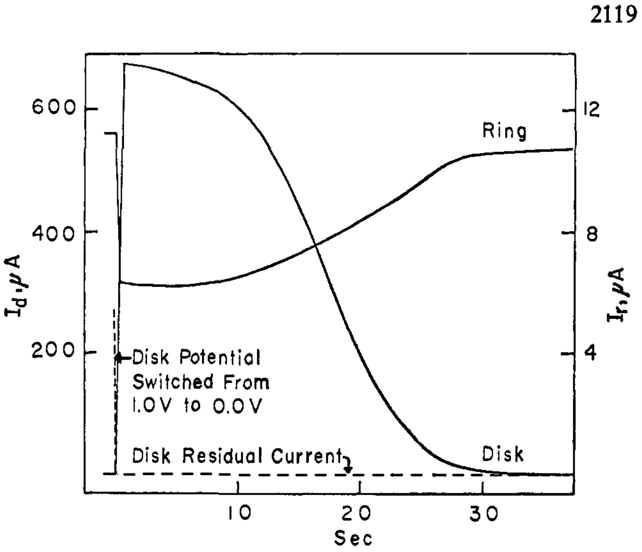

Figure 1. Time dependence of the oxygen reduction current at the disk, and the Cu(II) reduction current at the ring of a platinum ring–disk electrode. $C_{H_2SO_4} = 0.2\ M$, air saturated, and $C_{Cu(II)} = 2 \times 10^{-5}\ M$. Rotation speed = 2500 rpm. Electrode parameters: area of disk = 0.458 cm^2, collection efficiency = 0.183, and $\beta^{2/3} = 0.36$. Disk potential = 0.00 V *vs.* sce, $t > 0$; ring potential = -0.25 V at all t.

Since traces of copper are generally present in nearly all supporting electrolytes, and distilled water, even after all but the most heroic measures,[6] it occurred to us to investigate the correlation between the inhibition of the oxygen reduction current and the surface coverage of the platinum electrode resulting from the deposition of copper at underpotential.

Using the rrde in a solution containing $0.2\ M$ H_2SO_4 and $2 \times 10^{-5}\ M$ Cu(II), we stepped the disk electrode potential from the activation potential, $+1.0$ V, to 0 V and recorded the disk current and ring current (ring electrode potential equals -0.25 V) as a function of time. At these potentials the disk current results from oxygen reduction and the ring current from the reduction of Cu(II) and a contribution from the irreversible reduction of oxygen at a current less than 1% of the limiting convective-diffusion value.

Figure 1 shows the results of this experiment. The convective-diffusion current for the reduction of oxygen decreases as copper deposits at underpotential on the platinum disk electrode. Concurrently, there is a decrease in the "shielding"[7] of Cu(II) reaching the ring electrode.

While copper is being deposited at underpotential, the convective-diffusion-controlled current at the ring electrode, for Cu(II) reduction, i_r, is initially $i_d(\beta^{2/3} -$

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(1) A. Damjanovic, M. A. Genshaw, and J. O'M Bockris, *J. Electrochem. Soc.*, **114**, 466, 1967.

(2) J. J. Lingane, *J. Electroanal. Chem.*, **2**, 296 (1961).

(3) L. Müller and L. N. Nekrasov, *Electrochim. Acta*, **9**, 1015 (1964).

(4) L. Müller and L. N. Nekrasov, *Dokl. Akad. Nauk, SSSR*, **149**, 437 (1964).

(5) G. W. Tindall and S. Bruckenstein, *Anal. Chem.*, 40, 1051 (1968).

(6) The concentrations of copper in HCl and HNO_3 according to manufacturer's specifications are 0.5 and 0.05 ppm, respectively. In H_2SO_4 we find 0.05 ppm of copper by stripping analysis. In purified water 0.2–0.0004 ppm of copper is reported by E. B. Sandell, "Colorimetric Metal Analysis," 3rd ed, Interscience Publishers, New York, N. Y., 1959, pp 17, 39.

(7) D. T. Napp, D. C. Johnson, and S. Bruckenstein, *Anal. Chem.*, **39**, 481 (1967).

N), where i_d is the limiting convective-diffusion current for reduction of Cu(II) to Cu at the disk electrode, N is the collection efficiency of the ring electrode, and $\beta^{2/3}$ is a geometric parameter of the rrde. When the ring electrode is completely unshielded, $i_r = \beta^{2/3}i_d$. For surface coverages between 0 and 1, i_r lies between $(\beta^{2/3} - N)i_D$ and Ni_d. Oxygen reduction is completely inhibited (within 99.9%) after 25 sec when one monolayer of zerovalent copper has deposited at underpotential on the disk electrode. The reciprocal of time required to reduce the oxygen reduction current to 50% of the convective-diffusion limiting current, $1/t_{50\%}$, is directly proportional to the square root of the rotation speed at constant concentration. For reasons which are not yet clear, $1/t_{50\%}$ is not quite a linear function of concentration at constant rotation speed.

Table I. Dependence of $t_{50\%}$ on Concentration and Rotation Speed

$C \times 10^6\ M$	Rpm	$1/t_{50\%}$, sec^{-1}
2	2,500	0.0082
6	2,500	0.0223
10	2,500	0.0345
20	2,500	0.0626
40	2,500	0.108
60	2,500	0.144
80	2,500	0.188
6	400	0.0092
6	1,600	0.0188
6	2,500	0.0224
6	3,600	0.0300
6	6,400	0.0384
6	10,000	0.0510
80	400	0.0782
80	1,600	0.164
80	2,500	0.189
80	3,600	0.227
80	6,400	0.294
80	10,000	0.352

The data in Table I and Figure 1 support the view that both oxygen and copper are reduced at the same sites on the electrode surface. For example, the oxygen reduction current is one-half its maximum value at the same time that $i_r = (\beta^{2/3} - N/2)i_D$.

We have obtained, qualitatively, similar results for the inhibition of O_2 reduction by silver deposited at underpotential.

Lead and bismuth have no detectable effects upon the oxygen reduction current.

The level of trace Cu(II) in common reagent grade laboratory reagents is sufficiently high to implicate it as a potential culprit in the inhibition of oxygen reduction at platinum. It seems appropriate to recommend that the level of copper and silver be below $10^{-8}\ M$ in experiments involving oxygen reduction studies to avoid the effects of copper and silver deposition at underpotential in experiments of less than an hour's duration.

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Photolysis of Diene–Iron Tricarbonyls. Evidence for Norbornadien-7-one

Sir:

Most attempts to prepare the norbornadien-7-one system have failed.[1] Two syntheses, however, were successful, and these resulted in the formation of dibenzonorbornadien-7-one[2] and (norbornadien-7-one)-iron tricarbonyl (**1**).[3] The latter compound represents the simplest, stabilized derivative of the parent compound, norbornadien-7-one (**2**), and the precursor to the elusive **2**. Little evidence has been forwarded for the intermediacy of a norbornadien-7-one in a reaction system, but the presence of such a system has been inferred from decomposition products.[1a–c,4] We wish to report here evidence for the existence of free norbornadien-7-one, a highly unstable, short-lived intermediate.

Ultraviolet irradiation of dilute solutions of **1** with a 450-W Hanovia lamp and quartz glassware resulted in a rapid depletion of starting material. The irradiations generally were carried out until all starting material had disappeared (in a representative case, a 0.3% ether solution at −78° took 3 hr). The results of these experiments are summarized in Scheme I.

When **1** was irradiated at room temperature, 0°, or −78°, benzene was detected in the reaction mixtures.[5] The amount of benzene found varied between 50 and 90% and depended upon the initial concentration of complex and length of irradiation. The reaction was accompanied by insoluble material, a mixture of iron residues, and highly colored organic polymer. When the photolysis was carried out at −78° in the presence of 1,3-diphenylisobenzofuran as trapping agent, 9,10-diphenylanthracene was isolated in 6% yield;[7] in addition, benzene was formed in 55% yield.[5]

Carrying out the irradiation at liquid nitrogen temperature in an ether–pentane–alcohol (EPA; 3:3:5) glass resulted in the formation of small quantities of quadricyclanone (**3**) (0.5–5%[8]). The appearance of a band at 1746 cm^{-1} in the crude reaction product[9] on infrared analysis indicated formation of **9**. Its presence was confirmed by the comparison of retention times on vapor phase chromatography (vpc)[6] with

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(1) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (c) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (d) S. Yankelevitch and B. Fuchs, *ibid.*, 4945 (1967).

(2) J. Meinwald and E. G. Miller, *ibid.*, 253 (1961).

(3) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **90**, 1655 (1968).

(4) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968); this paper is a recent one that infers a substituted norbornadien-7-one as an intermediate which gives rise to aromatic products.

(5) The presence of benzene was determined by using vapor phase chromatography (vpc)[6] and comparing the retention time with authentic material. Percentage compositions were estimated with a known quantity of toluene as an internal standard and comparing the results to mixtures of known composition.

(6) F & M Model 810 with flame ionization detector using a column 6 ft × 0.25 in. packed with 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P.

(7) 9,10-Diphenylanthracene was isolated by column chromatography on Florisil and shown to be identical in all respects with commercially available material (K & K Laboratories); yield based on 1,3-diphenylisobenzofuran.

(8) Percentage compositions were estimated on vpc[6] by adding a known quantity of acetophenone to the solution following irradiation; results were compared to mixtures of known composition; the variable nature in yield was not looked into.

(9) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 1270 (1964).