

In aqueous methanol buffered with triethylamine and in the absence of silver salts, the chloride **5** was also converted predominately to ketone **3** (R = H). The first-order rate constant for the reaction (k_{150}) was $2 \times 10^{-5} \text{ sec}^{-1}$. This constant was invariant with increasing concentration of trimethylamine (up to a threefold excess).

It is, of course, possible that the accelerated rate of solvolysis of **5** is the result of complex formation between **5** and silver ion, and we are now studying this possibility. The complete absence of any observable reaction between Ag^+ and 2-chloro-3,3-dimethyl-1-butene, however, is evidence against a specific silver ion catalysis. We therefore interpret the foregoing observations, at present, in terms of the formation of an intermediate vinyl cation, **2**, which is stabilized through charge delocalization by the neighboring cyclopropane ring.⁸ This interpretation is supported by the non-rearranging tendency of the intermediate, which leads to products which still possess the cyclopropane ring (e.g., **3**, R = H, 1-cyclopropylethenyl acetate (**6**), and cyclopropylacetylene).

Further studies on cyclopropylethenyl derivatives with particular reference to the effect of ring substituents are now under way.

Acknowledgment. We thank Dr. R. G. Bergman of the California Institute of Technology for interesting discussions and for making his results available to us before publication. We also thank Professor Dr. C. J. Collins of the University of Tennessee for stimulating discussions.

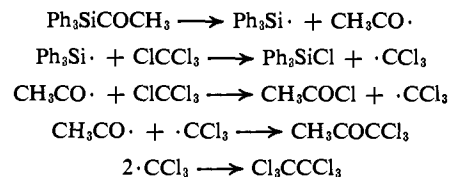
Michael Hanack, Tilmann Bässler
Chemisches Institut der Universität Tübingen
Tübingen, Germany
Received February 12, 1969

The Optical Stability of Asymmetric Silyl Radicals

Sir:

Recent studies in these laboratories suggest that the photolyses of certain acylsilanes in nonpolar solvents involve Norrish type I cleavage of the acyl-silicon bond and the formation of radicals. Particularly compelling evidence for the intermediacy of silyl radicals¹ and a radical mechanism are the results of photolyses² under nitrogen in Pyrex glassware of solutions of acetyltriphenylsilane in carbon tetrachloride, in which triphenylchlorosilane (88%), acetyl chloride (45%), 1,1,1-trichloropropanone (15%), and hexachloroethane (45% based on the formation of 2 mol of $\cdot\text{CCl}_3$ radical/mol of acetylsilane) were isolated. Photolysis of acetyl-

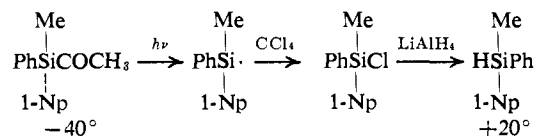
triphenylgermane gave similar products. A reasonable mechanism for the formation of these products is as follows.



The abstraction of chlorine from carbon tetrachloride by acyl radicals has been observed previously⁴ as has the abstraction of halogen by silyl radicals.^{1,5} Since the above reaction occurred quite rapidly (1 g of acetyltriphenylsilane was completely photolyzed in less than 40 min) it is probable that the radical intermediates are formed in high concentration, so it is not surprising that the coupling processes represented by the last two equations occur to a significant extent.

Because of the possible intermediacy of silyl radicals it seemed of interest to photolyze optically active acylsilanes in carbon tetrachloride since this could result in the generation of chiral silyl radicals. Photolysis of (-)-acetyl-1-naphthylphenylmethylsilane⁶ in carbon tetrachloride led to the rapid disappearance of ketone and the isolation of 69% of 1-naphthylphenylmethylchlorosilane, bp 160° (0.5 mm) (Kugelrohr), which had low positive rotations corresponding to optical purities of about 10–20%,⁷ together with acetyl chloride, 1,1,1-trichloropropanone, and hexachloroethane. This result suggested that if silyl radicals were being formed they were retaining at least some asymmetry prior to the abstraction of chlorine from the solvent, as proposed recently for a process which may also involve chiral silyl radicals.⁵ It also suggests that the abstraction process occurs, as expected, with retention of configuration since (-)-acetylsilane and (+)-chlorosilane have the same relative configurations.^{6,7}

Since it seemed highly probable that the low rotation of the chlorosilane was the result of racemization during the reaction or work-up, other runs were carried out in which the crude photolysate was immediately treated with lithium aluminum hydride in diethyl ether in order to convert the chlorosilane to silane, a reaction known to occur with high stereospecificity and to involve inversion of configuration. From two separate runs the 1-naphthylphenylmethylsilane, purified by chromatography of the crude reaction mixture on silica gel but not crystallized (to avoid possible enhancement of the optical purity), was found to have $[\alpha]^{25\text{D}} +18.1$ and $+21.3^\circ$, corresponding to 54 and 64% optical purities, respectively.



(1) S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometal. Chem.*, **15**, P17 (1968); A. Sitzki and K. Rühlmann, *Z. Chem.*, **8**, 427 (1968); G. A. Razuvaev, Yu. A. Alexandrov, V. N. Glushakova, and G. N. Figurova, *J. Organometal. Chem.*, **14**, 339 (1968); J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc., A*, 510 (1968); R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc., C*, 2559 (1967); D. Cooper, *J. Organometal. Chem.*, **7**, 26 (1967); L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **85**, 2662 (1963); J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4654 (1957).

(2) The photolyses employed a Westinghouse PAR 38 100-W mercury spotlight which emits virtually no wavelengths below 350 m μ . Acetylsilanes and -germanes have an n- π^* absorption in the region 370–380 m μ .³

(3) A. G. Brook, D. G. Anderson, J. M. Duff, P. F. Jones, and D. M. MacRae, *J. Am. Chem. Soc.*, **90**, 1076 (1968).

(4) S. Winstein and F. H. Neubold, Jr., *ibid.*, **69**, 2916 (1947).

(5) H. Sakurai, M. Murakami, and M. Kumada, *ibid.*, **91**, 519 (1969).

(6) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *ibid.*, **89**, 431 (1967).

(7) For information on the absolute configurations and optical rotations of a great number of optically active organosilicon compounds see L. H. Sommer "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

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.

Acknowledgment. This research was supported by the National Research Council of Canada.

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

A. G. Brook, J. M. Duff⁸

Department of Chemistry, University of Toronto
Toronto 5, Canada

Received January 31, 1969

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 H₂SO₄ and 2 × 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 ~+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 de-

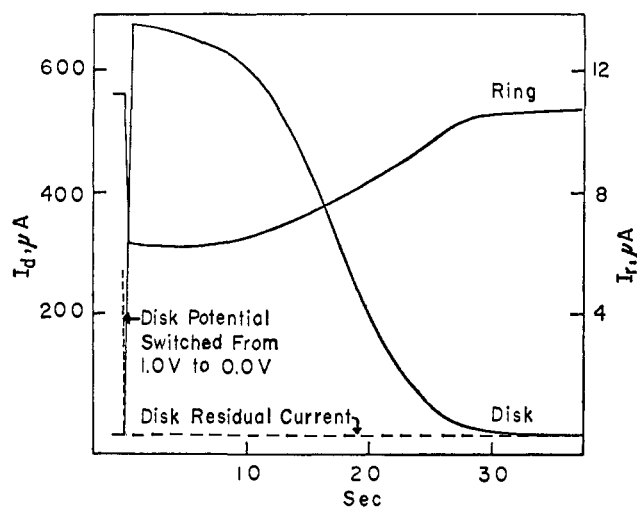


Figure 1. Time dependence of the oxygen reduction current at the disk, and the Cu(II) reduction current at the ring of a platinum ring-disk electrode. $\text{H}_2\text{SO}_4 = 0.2 \text{ M}$, air saturated, and $\text{C}_{\text{Cu(II)}} = 2 \times 10^{-5} \text{ M}$. Rotation speed = 2500 rpm. Electrode parameters: area of disk = 0.458 cm², 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 .

posited 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.

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 H₂SO₄ and 2 × 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 $i_d(\beta^{2/3} -$

(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 HNO₃ according to manufacturer's specifications are 0.5 and 0.05 ppm, respectively. In H₂SO₄ 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).