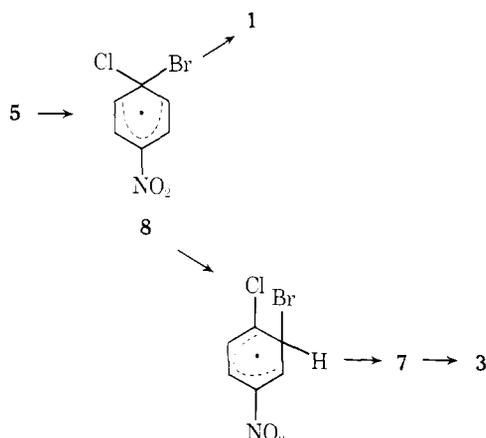


the same rate also produces **2** as the major product (49% at 58% reaction) plus some **3** (8% of **2** at 58% reaction), **1**, **6**, and **7**, and traces of other unidentified products.<sup>4,8</sup> Chlorodebromination and chlorodenitration are competitive. During the reaction, the concentration of **1** continually increased (followed through 76% consumption of **5**), but that of **6** passed through a maximum at about 13% reaction.<sup>4</sup> The production of the rearrangement product, **7**,<sup>8</sup> and the greater proportion of **3** from the reaction of **5** than of **1** are particularly significant to the question of ipso intermediates.

The rearrangement product, **7**, appears to require an ipso intermediate, **8**. The product proportions reveal that loss of



bromine atom (to form **1**) is the principal fate of **8**, but some bromine migration to the ortho position does occur. The substantially increased ratios of **3:2** from **5** than from **1** strongly imply that much of **7** reacts further by ipso attacks to produce **3** more readily than **3** is produced from **2**. The actual amount of rearrangement of ipso intermediate **8**, therefore, probably exceeds by severalfold the amount of **7** detected in the reaction mixtures.<sup>10</sup>

We believe that these data establish the formation and rearrangement of an ipso intermediate in these aromatic free-radical chlorinations.

## References and Notes

- Presented in part at the 33rd Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec. 1977, Abstract No. 175.
- For a review, with references, see R. B. Moodie and K. Schofield, *Acc. Chem. Res.*, **9**, 287 (1976).
- (a) A. Elbner, *Ber.*, **36**, 1229 (1903); (b) G. L. Goerner and R. C. Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951); (c) W. Voegtli, H. Muhr, and P. Lauger, *Helv. Chim. Acta*, **37**, 1627 (1954); (d) R. M. Noyes, *J. Am. Chem. Soc.*, **70**, 2614 (1948); (e) B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *ibid.*, **84**, 158 (1962); (f) J. R. Shelton and C. W. Uzelmeier, *Recl. Trav. Chim. Pays-Bas*, **87**, 1211 (1968); (g) P. Gouverneur and J. P. Soumillon, *Tetrahedron Lett.*, 133 (1976).
- B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957). These authors reported that *p*-bromochlorobenzene undergoes free-radical chlorodebromination 91% as rapidly as does bromobenzene but that *p*-bromonitrobenzene does not react under the same conditions.
- J. G. Traynham, *Tetrahedron Lett.*, 2213 (1976).
- J. G. Traynham, 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct. 1976, Abstract No. 376.
- R. D. Gandour and J. G. Traynham, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstract No. ORGN-137.
- At room temperature, ~80% of the halobenzene had been consumed after 161 h; at reflux temperature ~98% had been consumed after 34.5 h. For the room temperature process, the mass balance was 90–99% up to 57% reaction (121 h). The reactions are photoinitiated: gas chromatographic (GC) analysis of solutions of chlorine and **1** or **5** in carbon tetrachloride kept

in the dark at room temperature for 121 h showed no evidence of reaction products.

- Product **7** and its isomer, 1-bromo-2-chloro-4-nitrobenzene, were not distinguishable on three different GC columns at several different temperatures. The phenols derived from them by hydrolysis (replacement of halogen para to nitro) did have different retention times, and hydrolysis of the product mixture from **5** produced 2-bromo-4-nitrophenol but no 2-chloro-4-nitrophenol.
- GC analyses of product mixtures from **5** excluded the presence of 1,2-dichloro-4-nitrobenzene, 2,4-dichloro-1-nitrobenzene, and 1,4-dichloro-2-nitrobenzene, compounds which would have indicated chloro or nitro migration in ipso intermediates.

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## Heterogeneous Photocatalytic Preparation of Supported Catalysts. Photodeposition of Platinum on TiO<sub>2</sub> Powder and Other Substrates

Sir:

We recently described the use of platinumized TiO<sub>2</sub> powders in the heterogeneous photocatalytic decomposition of acetic (or other carboxylic) acids to methane (or the corresponding alkanes).<sup>1</sup> These powders were prepared by a heterogeneous photocatalytic deposition of metal to produce a supported metal catalyst. This unique and simple method of preparation produces materials consisting of finely dispersed metal on a semiconductor support which have also been found to be useful catalysts for other processes. We describe here the preparation of catalysts of this type and discuss possible extensions and applications. There have been previous reports of photoinduced metal deposition on semiconductors.<sup>2–5</sup> For example, the photovoltaic plating of silver or copper on the n side of a Si p–n junction has been described.<sup>2</sup> Photoreduction of Ag<sup>+</sup> and Pd<sup>2+</sup> on n-TiO<sub>2</sub><sup>3,4</sup> and Cu<sup>2+</sup> on n-TiO<sub>2</sub> and n-SrTiO<sub>3</sub> electrodes<sup>5</sup> has also been investigated, frequently in connection with photographic studies. To our knowledge no previous description of these processes at dispersed powders or the application of materials prepared in this manner as catalysts has been reported.

In a typical experiment for photodeposition of metallic platinum on TiO<sub>2</sub> powder, 2.02 g of lightly doped anatase powder produced from undoped anatase (MCB, >99% pure by x ray; particle size 125–250 μm by sieves; grain size ~0.2 μm by scanning electron microscopy (SEM)<sup>1b</sup>) was suspended in a mixture of 10 mL of platinizing solution (0.1 M hexachloroplatinic acid in 0.1 M hydrochloric acid), which had been neutralized with sodium carbonate and then brought to a pH of ~4 by addition of acetic acid. This suspension was thoroughly flushed with nitrogen to remove oxygen and CO<sub>2</sub> and heated to 55 ± 3 °C. The reaction mixture was irradiated with a 2500-W Hg–Xe lamp, operated at 1600 W, while a slow stream of N<sub>2</sub> carried the evolving CO<sub>2</sub> into a saturated solution of Ba(OH)<sub>2</sub> in 1 M NaOH, to form a precipitate of BaCO<sub>3</sub>. After 3.6-h irradiation at 55 °C a considerable amount of BaCO<sub>3</sub> was trapped (after workup, 257 mg or 1.32 mmol, corresponding to an average rate of CO<sub>2</sub> evolution of ~400 μmol/h); the color of the originally bright orange solution had largely faded and the grayish powder had darkened significantly. A black spot of Pt was also noticed at the inside of the cell wall where the light beam was incident. Transfer of the reaction mixture, removal of reaction solution followed by repeated washing of the powder with distilled water, and finally

drying at 120 °C for 14 h yielded 2.119 g of dark gray solid. The dark deposits were shown by ESCA to be Pt<sup>0</sup>, with only the two signals of zero-valent Pt at 75.4 (4f<sup>5/2</sup>) and 71.85 (4f<sup>7/2</sup>) eV present.<sup>6</sup> The distribution of platinum was fairly uniform; no agglomerates could be detected with SEM. Similar photoplatinization of white, undoped anatase<sup>7</sup> and faint yellow tungsten oxide (WO<sub>3</sub>) could also be accomplished. The mechanism of the photodeposition probably follows that found in other heterogeneous photoprocesses at semiconductors.<sup>1</sup> The photogenerated hole causes oxidation of acetate while the photogenerated electron leads to reduction of the platinum complex. The irreversibility of the oxidative decarboxylation of the acetate<sup>8</sup> hinders any back-reaction between the reduced metal species and oxidation product and suggests that carboxylic acids are excellent choices as electron donors for heterogeneous photoreductions.

To study the role of the electron donor in the process a similar suspension of lightly doped anatase in a solution of sodium hexachloroplatinum(IV), pH ~6, at 60 °C was irradiated in the absence of acetate. The deposition of metal was obviously slower, but after irradiation for 21 h the powder had darkened significantly and after separation had gained 62 mg of weight (total weight, 962 mg), presumably owing to deposition of metallic platinum. In this case water plays the role of donor and is oxidized, less efficiently, at the illuminated particle.

A homogeneous photodecomposition of the platinum(IV) complex in the presence of acetic acid was also found. Irradiation of a homogeneous deaerated, buffered mixture of 7.5 mL of H<sub>2</sub>PtCl<sub>6</sub> (~0.11 M) and 7.5 mL of glacial acetic acid at pH 4 led to deposition of a metallic mirror of platinum on the cell wall together with evolution of CO<sub>2</sub>. After 13.4 h, 0.89 mmol of CO<sub>2</sub> had been trapped as BaCO<sub>3</sub> and 131 mg (0.67 mmol) of metallic Pt had been photodeposited. The solution color first changed from bright orange to bright red (after ~7 or 8 h, no black solids were present) and was a faint orange at the end of the photolysis. The photodeposited Pt was found to give again only the two ESCA signals of zero-valent Pt (74.8 and 71.4 eV). The homogeneous photodeposition permitted the photoplatinization of aluminum oxide (Woelm, neutral), a material whose wide band gap (>7 eV) prevents light absorption by the solid.<sup>9</sup> The mechanism of this homogeneous process was not investigated; similar photoreductions of platinum(IV) complexes to platinum(II) involving coordinated oxalate or malonate have been reported,<sup>10</sup> but reduction to the metal was not found.

Our reasons for proposing different heterogeneous and homogeneous routes to metal deposition are based on the following: (a) the rate of CO<sub>2</sub> evolution in the presence of TiO<sub>2</sub> (~400 μmol/h) is much larger than in equivalent Al<sub>2</sub>O<sub>3</sub> suspensions (~47 μmol/h) or in the absence of powder (~66 μmol/h); (b) the Pt deposition rate under homogeneous conditions is slower by a factor of ~2; (c) the ratio of Pt deposited to CO<sub>2</sub> evolved, 2.6:1 in the presence of TiO<sub>2</sub> (compared with a predicted complete heterogeneous deposition ratio of 4:1), is greater than the ratio in the absence of powder (1.3:1) or with Al<sub>2</sub>O<sub>3</sub> present (0.8:1); (d) the homogeneous process is characterized by a long induction period where no Pt deposition occurred while deposition of metallic Pt was noticed in the TiO<sub>2</sub> experiments within 25 min. Finally we have observed conditions, such as for the deposition of Cu on TiO<sub>2</sub><sup>7</sup> (see below), where no homogeneous deposition process occurs.

This general method of catalyst preparation is of interest because high dispersion and small clusters of the metal on the support surface should exist. Metal deposition probably only occurs near sites where photons strike the surface and the light flux can be made very small. The low temperature conditions of the photodeposition also would minimize surface diffusion of metal atoms which would produce larger aggregates. There

is a potentially wide range of metals that might be photodeposited on semiconductor powders by this method. For aqueous suspensions of TiO<sub>2</sub>, M<sup>+n</sup>/M couples with redox potentials positive of the H<sup>+</sup>/H<sub>2</sub> potential (which corresponds closely to the flat-band potential of n-TiO<sub>2</sub>) should be available, with a wider range possible in nonaqueous solvents. In recent experiments<sup>7</sup> PdCl<sub>4</sub><sup>2-</sup>, Ag<sup>+</sup>, and Cu<sup>2+</sup> have been photocatalytically reduced and deposited as metals on undoped anatase powder in the presence of acetate, with evolution of CO<sub>2</sub>. Several experiments have demonstrated the use of these powders as catalysts. For example, platinized TiO<sub>2</sub> and WO<sub>3</sub> powders showed high catalytic activity for the thermal hydrogenation of neat benzene (and cyclohexene) to cyclohexane at temperatures of 80 °C and below. Similarly the platinized anatase powders did result in efficient photocatalytic decarboxylation of saturated carboxylic acids.<sup>1</sup> Besides the possibility of forming highly active, solid supported metal catalysts, the photodeposition of metals on solid substrates is attractive for light controlled metal deposition (e.g., in printed circuits) and for treatment of some waste streams (e.g., those containing low levels of Cu<sup>2+</sup>).<sup>11</sup> Research extending the scope of the photodeposition of metals on solids and concerning their catalytic activity now is in progress in this laboratory.<sup>12</sup>

## References and Notes

- (1) (a) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978); (b) *ibid.*, in press.
- (2) J. I. Pankove in "The Electrochemistry of Semiconductors", P. J. Holmes, Ed., Academic Press, New York, N.Y., 1962, p 316.
- (3) F. Mollers, H. J. Tolle, and R. Memming, *J. Electrochem. Soc.*, **121**, 1160 (1974).
- (4) (a) H. Jonker, C. J. G. F. Janssen, C. J. Dippel, Th. P. E. W. Thijssens, and L. Postma, *Photogr. Sci. Eng.*, **13**, 45 (1969); (b) G. L. McLeod, *ibid.*, **13**, 93 (1969); (c) E. J. Delorenzo, L. K. Case, E. M. Stickless, and N. A. Stamoulis, *ibid.*, **13**, 111 (1963); (e) D. Vohl, *ibid.*, **13**, 120 (1969).
- (5) M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, *J. Solid State Chem.*, **22**, 17 (1977).
- (6) Literature values from "CRC Handbook of Spectroscopy", J. W. Robinson, Ed., CRC Press, Cleveland, Ohio, 1974: Pt<sup>0</sup>, 4f<sup>5/2</sup> (74.0 eV); PtO, 4f<sup>5/2</sup> (76.6 eV), 4f<sup>7/2</sup> (73.3 eV); PtO<sub>2</sub>, 4f<sup>5/2</sup> (77.4 eV), 4f<sup>7/2</sup> (74.1 eV).
- (7) W. Dunn, B. Kraeutler, and A. J. Bard, unpublished results.
- (8) In the gas phase at 65 °C the acetoxy radical has been measured to decarboxylate with a half-life time of 10<sup>-10</sup> s: W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).
- (9) The ESCA signals for Al<sub>2</sub>O<sub>3</sub> overlap those of Pt; computer subtraction of the Al<sub>2</sub>O<sub>3</sub> background gave two signals at 73.5 and 77.9 eV whose position did not change upon exposure of the photoplatinized Al<sub>2</sub>O<sub>3</sub> powder to hydrogen at 300 °C. A shift of the Pt signals to slightly higher energies because of the properties of the support appears possible.
- (10) T. Banerjee, H. Chakravorty, and S. Sarker, *J. Indian Chem. Soc.*, **20**, 207 (1943).
- (11) (a) K. B. Keating and J. M. Williams, *Resour. Recovery Conserv.*, **2**, 39 (1976). (b) Photocatalytic removal of CN<sup>-</sup> on TiO<sub>2</sub> and other powders was suggested in S. N. Frank and A. J. Bard, *J. Phys. Chem.*, **81**, 1484 (1977).
- (12) Support by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung to B.K. is gratefully acknowledged.

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## Intramolecular Antiferromagnetic Exchange in Tris(o-semiquinone) Complexes of Vanadium(III), Chromium(III), and Iron(III)

Sir:

Examples of transition metal complexes containing paramagnetic ligands are relatively few in number. Complexes consisting of both paramagnetic metal ions and paramagnetic ligands are of particular importance for the fundamental information they offer about metal-ligand bonding and specifically about interactions between metal centers and paramagnetic organic substrate molecules. Spin-spin exchange