Platinum Hydrosols in the Sensitized Photoreduction of Water

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Summary Pt hydrosols (22 Å diameter) catalyse H_2 evolution from water with nearly 100% efficiency in the light-induced redox reaction which involves the $Ru(2,2'\text{-bipyridine})_3{}^{2+}$–methyl viologen–ethylenediaminetetra-acetate model system; the catalytic step is not rate-determining.

CATALYTIC studies on hydrosols of transition metals and their oxides have been of considerable interest recently because of their relevance to the photochemical decomposition of water. Investigations[1–3] of platinum hydrosols as the fourth component of a $Ru(bpy)_3{}^{2+}$–MV^{2+}–EDTA (bpy = 2,2′-bipyridine; MV^{2+} = methyl viologen; EDTA = ethylenediaminetetra-acetate) hydrogen-evolving model system have been contradictory with respect to the effect of particle size on the catalytic activity and the extent of catalytic specificity.

A necessary requirement for a catalyst under fixed conditions to function at maximum effectiveness in a specific conversion process as part of a series of coupled chemical events is that the catalytic step is not rate-determining. In the $Ru(bpy)_3{}^{2+}$–MV^{2+}–EDTA model system the catalytic step is shown to be no longer rate-determining when the mean diameter of Pt colloids is reduced from 50 to 20 Å. Rate data normalized to constant light intensity (*i.e.*, quantum yields) determined from initial rates are consistent with the catalytic step being nearly 100% efficient in converting the reductive power of the electron relay, MV^+, into H_2.

Pt hydrosols were synthesized by reducing H_2PtCl_6 with $NaBH_4$ in basic solution and then buffering to pH 5 or 6. During the preparations, 0·5% polyethyleneglycol (*M* of PEG, 15000—20000) was added. Particle sizes were measured by transmission electron microscopy.

Solutions containing $Ru(bpy)_3{}^{2+}$, MV^{2+}, EDTA, and Pt catalyst were irradiated with monochromatic light and the volume of gas evolved was monitored with a gas microvolumeter.[4] The formation rate of MV^+ (Figure) was determined by monitoring the temporal growth of the 602 nm absorption band (E 11900 mol l^{-1} cm^{-2}).

The Pt hydrosols consisted of spherical particles with a distribution of diameters between 15 and 30 Å and an average diameter of 22 Å, corresponding to a mean aggregation number of 370 Pt atoms per particle. At a typical

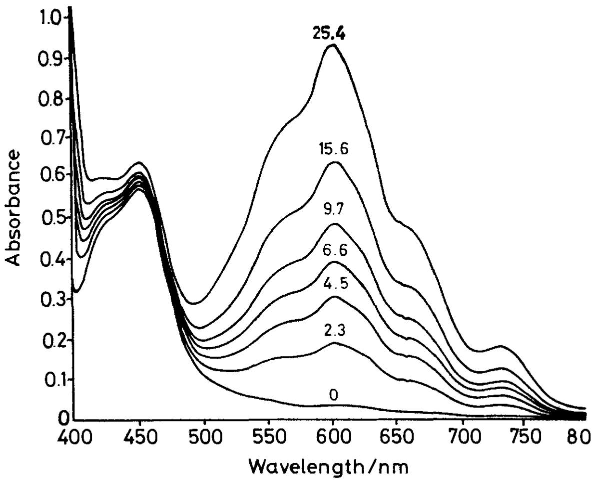

FIGURE. Absorption spectra of photolysed solution (2·0 ml) containing $Ru(bpy)_3Cl_2$ (4×10^{-5} M), methyl viologen ($2{\cdot}0 \times 10^{-3}$ M), Na_2EDTA (0·01 M), and acetate buffer (0·05 M) at pH 5; λ 436 ± 5 nm. Duration of photolysis given in seconds on each curve; $I_0 = 1{\cdot}27 \times 10^{-7}$ E s^{-1}; 23·6 ± 0·1 °C.

atomic Pt concentration of $6{\cdot}4 \times 10^{-5}$ mol l^{-1}, the colloid concentration was $1{\cdot}7 \times 10^{-7}$ mol l^{-1} with a contact area of 1500 Å^2 per particle ($1{\cdot}3 \times 10^6$ cm^2 g^{-1}).

The Pt particles can be considered analogous to microplatinum cathodes.[5] Reduction of the Pt particles by MV^+ results in the establishment of a rapid equilibrium between protons (or water molecules) in solution and the microplatinum electrodes, in a manner similar to those proposed for silver[6] and gold[6,7] hydrosols.

The mechanism of H_2 evolution in the $Ru(bpy)_3^{2+}$–MV^{2+}–EDTA model system has been well studied.[8] Reaction (1) describes the conversion of MV^+ into hydrogen. From

$$MV^+ + H_2O \xrightarrow[\text{Pt catalyst}]{} MV^{2+} + \tfrac{1}{2}H_2 + OH^- \qquad (1)$$

equation (1) it is evident that an upper limit of ϕ_{H_2} is $\phi_{MV^+}/2$.

As the concentration of atomic Pt is increased, the size of the hydrosol is augmented, and the catalytic activity is reduced. At $2{\cdot}6 \times 10^{-4}$ g-atoms l^{-1}, Pt particles of 50 Å diameter form as clusters of still larger aggregates. In the case of these 50 Å hydrosols, the value of ϕ_{H_2} (0·0271) at pH 5 is about half that measured for the more dilute solutions ($6{\cdot}4 \times 10^{-5}$ g-atoms l^{-1}) which contain particles of 22 Å diameter. Besides the concentration effect, low pH, H_2 bubbling, or *in situ* photochemical generation of H_2 tend to produce larger aggregates.

The largest value of ϕ_{H_2}, $0{\cdot}059 \pm 0{\cdot}006$, was obtained with particles of 22 Å diameter at pH 5. While this value is in disagreement with an earlier determination,[1] it is consistent with more recent estimates[9] of ϕ_{H_2} 0·05 to 0·10. In the determination of ϕ_{H_2}, the light intensity absorbed by the sensitizer $Ru(bpy)_3^{2+}$ was corrected for light scattering by the Pt particles.

In separate experiments involving the same system, but without the catalyst, ϕ_{MV^+} was determined to be $0{\cdot}108 \pm 0{\cdot}005$. Thus, during the initial stages of H_2 evolution, the MV^+ and H_2 production rates are in a ratio (2 : 1) consistent with reaction (1), indicating that the catalysis is not rate-determining under the stated experimental conditions. The rate-determining reaction occurs before catalysis and is associated with the *net* production of MV^+. Based on *initial* mass balance, no evidence exists for the H_2-competing hydrogenation reaction of methyl viologen reported by others.[2,3] As the reaction proceeds, however, the 2 : 1 stoicheiometric ratio of MV^+ to H_2 is altered. In part, this change in stoicheiometry must be associated with the accumulation of adsorbed H-atoms on the Pt surface and the competing hydrogenation reaction. Elimination of the MV^+ electron-relay pathway is, consequently, required to improve the long-term H_2 production efficiency.

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