J. Am. Chem. Soc. **1982**, *104*, 422-425

In Vitro Analogues of Photosystem II. Combined Flash Photolytic and Conductometric Study of Light-Induced Oxygen Evolution from Water Mediated by Colloidal RuO_2/TiO_2

Robin Humphry-Baker, Jochen Lilie,[†] and Michael Grätzel[*]

Contribution from the Institut de Chimie Physique, Ecole Polytechnique Fêdêrale, 1015 Lausanne, Switzerland. *Received March 2, 1981.*
Revised Manuscript Received June 22, 1981

Abstract: Colloidal TiO_2 particles (R_h = 200 Å) when charged with ultrafine deposits of RuO_2 are extremely active catalysts for water oxidation. A photochemical model system consisting of aqueous $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ solutions is used to probe the mechanistic details of the oxygen evolution reaction $4Ru(bpy)_3^{3+} + 2H_2O \rightarrow 4H^+ + O_2 + 4Ru(bpy)_3^{2+}$. Application of combined flash photolysis and conductance techniques shows that hole transfer from $Ru(bpy)_3^{3+}$ to the catalyst and proton release from water decomposition occur simultaneously and within milliseconds at 3 mg of RuO_2/L. Mechanistic implications are discussed.

Water oxidation into molecular oxygen and protons by photosensitized electron transfer plays a primordial role in the conversion of sunlight into chemical energy. Irrespective of the detailed mechanism, this process requires the generation as well as cooperation of four redox equivalents of sufficient oxidizing power. Thus, photosystem II in green plant photosynthesis operates as a hole storage device releasing oxygen[1] and protons[2] in oscillatory fashion upon exposure to flashed light.

Recently it was discovered in our laboratory[3] that noble metal oxides such as PtO_2, IrO_2 and RuO_2 in powdered or colloidal form are capable of simulating the function of the water splitting enzyme (WSE) in photosystem II. These redox catalysts[4] achieve coupling of the one-electron reduction of a suitable acceptor (D^+) to water oxidation according to eq 1. This effect was subsequently exploited to develop systems affording cyclic and sustained water cleavage by four quanta of visible light.[5] In order to improve the efficiency of such devices, it is mandatory to scrutinize the kinetic and mechanistic aspects of the redox events involved in water decomposition. We wish to present here a combined flash photolytic and conductometric approach to probe the elementary steps of the oxygen evolution reaction.

$$4D^+ + 2H_2O \xrightarrow{\text{cat.}} 4H^+ + 4D + O_2 \qquad (1)$$

Experimental Section

$Ru(bpy)_3^{2+}$ dichloride (Strem) was used as supplied. Deionized water was refluxed with alkaline permanganate and subsequently distilled twice from a quartz still. All other chemicals were at least reagent grade and were used as supplied.

The colloidal TiO_2 particles (hydrodynamic radius 200 Å) were prepared via hydrolysis of titanium tetraisopropoxide in dilute HCl according to a procedure described earlier.[6] X-ray studies performed with the colloidal TiO_2 particles showed that the main part of the material is X-ray amorphous. The diffraction patterns indicate the presence of a small fraction of anatase. The TiO_2 is dried under vacuum to remove isopropyl alcohol and redispersed in water. Excess HCl is eliminated through treatment with AMBERLITE exchange resin, and polyvinyl alcohol (0.1% w/v) is added to stabilize the colloidal TiO_2 particles. The loading of these TiO_2 particles with RuO_2 has already been described.[6] The concentration of TiO_2 was 50–200 mg/L, and the loading with RuO_2 varied between 1 and 4%. This preparation is perfectly transparent and hence readily amenable to flash photolysis investigation. Moreover, it is active in cyclic water decomposition systems.[6]

Laser photolysis experiments were carried out with a frequency-doubled Nd laser (λ = 530 nm). The 20-ns (~50-mJ) pulse impinges on a cell equipped with optically flat windows and two planar electrodes allowing for simultaneous registration of changes in optical density and electrical conductivity. The relatively high electrolyte concentration in the solution requires the use of a fast AC conductance technique[7,8] with a time resolution of ca. 1 μs. The calibration of the conductivity cell was carried out by using an aqueous solution of $Ru(bpy)_3^{2+}$ in the presence of tetranitromethane as a reference system. Laser excitation of $Ru(bpy)_3^{2+}$ induces the reaction sequence

$$Ru(bpy)_3^{2+} + C(NO_2)_4 \xrightarrow{\text{fast}} Ru(bpy)_3^{3+} + NO_2 + C(NO_2)_3^- \qquad (2)$$

$$NO_2 + {}^1/_2H_2O \xrightarrow{\text{slow}} H^+ + {}^1/_2NO_3^- + {}^1/_2NO_2^-$$

In acid solution this is accompanied by the conductance change

$$\Delta K = f\sum c_i\lambda_i = fc[\lambda(Ru(bpy)_3^{3+}) + \lambda(C(NO_2)_3^-) + \lambda(H^+) + \tfrac{1}{2}\lambda(NO_3^-) + \tfrac{1}{2}\lambda(NO_2^-) - \lambda(Ru(bpy)_3^{2+})] \qquad (3)$$

where f is a constant and c_i and λ_i refer to the concentration and the equivalent conductance of the ions, respectively. The sum of equivalent conductances in parenthesis has the value 500 Ω^{-1} cm^2 M^{-1}. c is the

---

[†] On leave of absence from the Hahn Meitner Institute, Berlin.

(1) (a) M. Calvin, Photochem. Photobiol., **23**, 425 (1976); (b) M. Calvin and G. M. Androes, *Science* (Washington, D.C.) *138*, 867 (1962); (c) J. R. Bolton and D. O. Hall, *Annu. Rev. Energy*, **401**, 353 (1979). (d) P. Joliot and B. Kok in "Bioenergetics of Photosynthesis", Govindjee, Ed., Academic Press, New York, 1975, pp 387–412.

(2) W. Junge and W. Ausländer in "Photosynthetic Oxygen Evolution", H. Metner, Ed., Academic Press, New York, 1978, pp 312-328.

(3) (a) J. Kiwi and M. Grätzel, *Agnew. Chem., Int. Ed. Engl.*, **17**, 860, (1978); (b) J. Kiwi and M. Grätzel, *ibid.*, **18**, 624 (1979). (c) M. Grätzel in "Dahlem Conference on Light Induced Charge Separation 1978", H. Gerischer and J. J. Katz, Eds., Verlag Chemie, Weinheim/Berg Str., Germany, 1979, p 299.

(4) Recent papers on redox catalytic oxygen evolution from water include: (a) J. Kiwi and M. Grätzel, *Chimia*, **33**, 289 (1979); (b) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979); (c) K. Kalyanasundarm, O. Micic, E. Promauro, and M. Grätzel, *Helv. Chim. Acta*, **62**, 2432 (1979); (d) J. Kiwi, *Isr. J. Chem.*, **18**, 369 (1979); (e) V. Ya. Shafirovich, N. K. Khannov, and V. V. Strelets, *Nouv. J. Chim.*, **4**, 81 (1980); (f) E. Pramauro and E. Pelizzetti, *Inorg. Chim. Acta Lett.* **1980**, *45*, L131.

(5) (a) K. Kalyanasundaram and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **18**, 701 (1979); (b) J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca, and M. Grätzel, *ibid.*, **19**, 647 (1980); (c) E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *Nature* (*London*), **289**, 158 (1981); (d) M. Grätzel, *Ber. Bunsenges. Phys. Chem.*, **84**, 981 (1980). (e) E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *J. Am. Chem. Soc.* **1981**, *103*, 6324. (f) M. Grätzel, "Faraday Discussions on Photoelectrochemistry", Oxford, U.K., 1980. (g) K. Kalyanasundaram and M. Grätzel, Nato Summer School on Photoelectrochemistry, Gent 1980 (Belgium), Nato Advanced Studies Treatise. (h) K. Kalyanasundaram, E. Borgarello and M. Grätzel, *Helv. Chim. Acta*, **64**, 362 (1981).

(6) D. Duonghong, E. Borgarello, and M. Grätzel, *J. Am. Chem. Soc.* **1981**, *103*, 4685.

(7) J. Lilie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).

(8) G. Rothenberger, P. P. Infelta, and M. Grätzel, *J. Phys. Chem.*, **83**, 1871 (1979).

0002-7863/82/1504-0422$01.25/0 © 1982 American Chemical Society

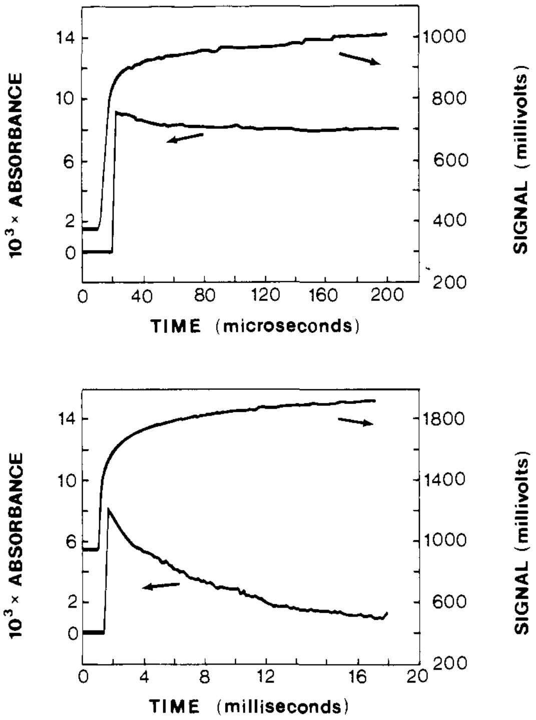


Figure 1. Laser photolysis experiments with solutions containing 10^{-4} M $Ru(bpy)_3^{2+}$ and 2×10^{-3} M $S_2O_8^{2-}$ (catalyst TiO_2 (200 mg/L) loaded with RuO_2 (3 mg/L) and simultaneous observation of transient conductance and absorbance.

concentration of nitroform anions and was determined from the absorbance change at 348 nm ($\epsilon(C(NO_2)_3^-) = 1.4 \times 10^4$ M^{-1} cm^{-1}). Thus the constant f can be evaluated.

Results and Discussion

The mechanism of intervention of colloidal RuO_2 as a mediator in oxygen generation from water was examined by using an aqueous solution of $Ru(bpy)_3^{2+}$ and peroxodisulfate as a model system. The photochemistry of this system has been previously examined in detail.[9,10] The excited state of $Ru(bpy)_3^{2+}$ is quenched oxidatively by $S_2O_8^{2-}$

$$^*Ru(bpy)_3^{2+} + S_2O_8^{2-} \xrightarrow{k_4} Ru(bpy)_3^{3+} + SO_4^- + SO_4^{2-} \quad (4)$$

the rate constant k_4 being 8×10^8 M^{-1} s^{-1} and the cage escape yield 100%. In a subsequent dark reaction a second $Ru(bpy)_3^{2+}$ is oxidized by SO_4^-

$$Ru(bpy)_3^{2+} + SO_4^- \xrightarrow{k_5} SO_4^{2-} + Ru(bpy)_3^{3+} \quad (5)$$

$k_5 \geq 10^9$ M^{-1} s^{-1}. Thus for every excited $Ru(bpy)_3^{2+}$ that undergoes quenching two $Ru(bpy)_3^{3+}$ are produced.

$$2Ru(bpy)_3^{2+} + S_2O_8^{2-} \xrightarrow{h\nu} 2Ru(bpy)_3^{3+} + 2SO_4^{2-} \quad (6)$$

Under our experimental condition the overall reaction (6) is completed within only a few microseconds after the laser pulse and occurs with a quantum yield of unity. Thus this system allows for the efficient and very rapid generation of $Ru(bpy)_3^{3+}$, whose reaction with water in the presence of colloidal RuO_2[11]

$$4Ru(bpy)_3^{3+} + 2H_2O \xrightarrow{RuO_2} 4Ru(bpy)_3^{2+} + 4H^+ + O_2 \quad (7)$$

is in the focus of our present investigation. This system has the further advantage that the photoreaction 6 is not affected by the solution pH and also does not produce any pH changes. Formation of protons can therefore be attributed unambiguously to the water oxidation process 7.

Figure 1 presents oscilloscope traces illustrating laser-induced conductance as well as absorbance changes observed with a solution containing 10^{-4} M $Ru(bpy)_3^{2+}$ and 2×10^{-3} M $S_2O_8^{2-}$ at pH 5 (adjusted with HCl). A wavelength of 640 nm was selected for monitoring formation and decay of $Ru(bpy)_3^{3+}$. Photolysis by analyzing light was prevented by using a 620-nm cutoff filter. Also the experiments were performed in the dark to avoid exposure to room light.[12] The upper oscillogram shows that both the 640-nm absorbance as well as the conductance increase steeply immediately after the laser pulse. The optical behavior is expected from the fast nature of reactions 4 and 5 leading to $Ru(bpy)_3^{3+}$ formation. The increase in conductivity can be predicted quantitatively by using the relation

$$\Delta K_1 = fc[\lambda(Ru(bpy)_3^{3+}) + \lambda(SO_4^{2-}) - \lambda(Ru(bpy)_3^{2+}) - \tfrac{1}{2}\lambda(S_2O_8^{2-})] \quad (8)$$

The sum of equivalent conductances in parentheses has the value[13] 160 Ω^{-1} cm^2 mol^{-1}; f was determined by calibration with the standard system as outlined above; c is the concentration of $Ru(bpy)_3^{3+}$ at the completion of the photoreaction and can be derived from the absorbance change at 640 nm.[14] Experimentally observed ΔK_1 values are in excellent agreement with this prediction, showing that the calibration of the cell was properly performed.

The behavior of the absorbance and conductance in the millisecond time domain is illustrated in the lower part of Figure 1. While the former decays back to the base line, the latter increases until it reaches a plateau from where on no further changes are noted. A first-order kinetic fit gives for both curves $k_{obsd} = 10^2$ s^{-1}. The slower component in the conductance rise is significantly larger than the initial fast increase. Denoting the height of the conductance signal in the plateau region as ΔK_2, one finds $(\Delta K_2 - \Delta K_1)/\Delta K_1 = 2 \pm 0.1$.

The increase in the conductance in the millisecond time domain reflects the formation of protons during water oxidation. From the stoichiometry of eq 7 this increment should correspond to

$$K_2 - K_1 = fc[\lambda(H^+) + \lambda(Ru(bpy)_3^{2+}) - \lambda(Ru(bpy)_3^{3+})] \quad (9)$$

As the sum of equivalent conductances in parentheses equals 310, the ratio $(\Delta K_2 - \Delta K_1)$ ΔK_1 is expected to be ~2, which corresponds exactly to the experimental result.

A series of experiments was performed to establish the effect of RuO_2 loading, pH, and catalyst concentration on the rate of water oxidation by $Ru(bpy)_3^{3+}$. Maintaining the TiO_2 concentration at 200 mg/L and the pH at 3.6, we first investigated catalysts charged with different amounts of RuO_2 (1–4%). Between 2 and 4% of RuO_2 there is no effect of loading on the water oxidation rate. The latter decreases about 3 times upon reducing the loading to 1%. No water oxidation at all could be observed with solutions containing the TiO_2 carrier material alone, i.e., in the absence of RuO_2. Here, after the initial increase due to photoreaction 6 there is no further change in the conductivity or optical absorbance of the solution over a time scale of at least several seconds. This shows that TiO_2 alone is catalytically inactive and RuO_2 loading is required to afford water oxidation by $Ru(bpy)_3^{3+}$.

For a test of the effect of pH, experiments were performed with a colloidal catalyst containing 2% of RuO_2. This was employed at a concentration of 200 mg/L. Figure 2 shows that the rate of water oxidation increases markedly with OH^- concentration. A linear relation between log k_7 and pH is observed in the region

---

[9] F. Boletta, A. Juris, M. Maestri, and D. Sandrini, *Inorg. Chim. Acta*, **44**, L175 (1980).

[10] M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel, and M. Grätzel, *Helv. Chim. Acta*, **63**, 1111 (1980).

[11] For uncatalyzed oxygen production from $Ru(bpy)_3^{3+}$ see: C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975). From porphyrines Cf. G. Porter, *Proc. R. Soc. London, Ser. A*, *362*, 281 (1978); A. Harriman and G. Porter, U.S. Patent 4176026 (1979).

[12] This leads to depletion of $S_2O_8^{2-}$. RuO_2-catalyzed decomposition of $S_2O_8^{2-}$ is negligible during the time period of the experiment.

[13] Tabulated values are $\lambda(H^+) = 350$ and $\lambda(SO_4^{2-}) = 160$ Ω^{-1} cm^2 mol^{-1}. For the other ions λ was taken as 40 Ω^{-1} cm^2 mol^{-1} per charge which is typical for ions of this size.

[14] An extinction coefficient of 325 M^{-1} cm^{-1} was used for $Ru(bpy)_3^{3+}$ at 640 nm.

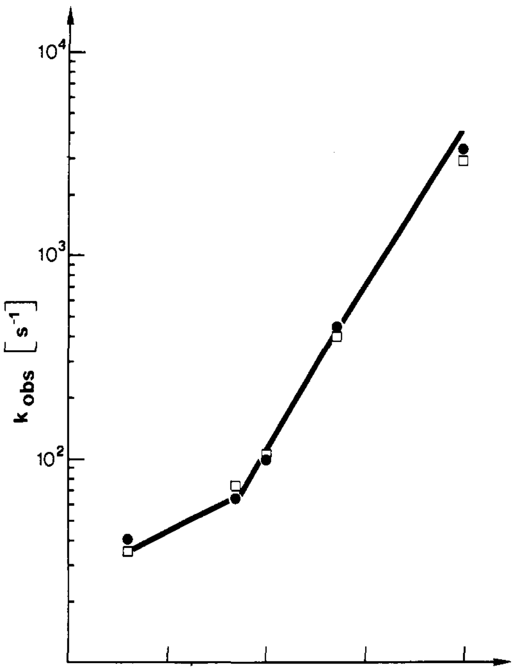


Figure 2. Effect of pH on the observed rate constant for water oxidation by $Ru(bpy)_3^{3+}$ (catalyst 200 mg of TiO_2 loaded with 2% of RuO_2): ●, conductance increase: □, absorbance decay.

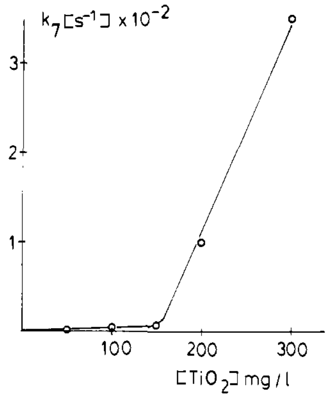


Figure 3. Effect of catalyst concentration on the observed rate constant for water oxidation by $Ru(bpy)_3^{3+}$ (colloidal TiO_2 charged with 2% RuO_2; pH 5).

from pH 4.5 to pH 6. At lower pH the k_7 values are higher than those expected from the extrapolation of this straight line. Above pH 5.6 the rate of water oxidation appears to increase further. However, these data have to be viewed with caution as the change in the solution pH during reaction 7 is significant in this domain. Note that throughout the investigated pH region the decay of $Ru(bpy)_3^{3+}$ occurs at the same rate as the appearance of H^+.

Finally, the effect of catalyst concentration on the water oxidation rate was investigated. These experiments were performed at pH 5 by using colloidal TiO_2 loaded with 2% RuO_2 as a catalyst. A plot of k_7 vs. catalyst concentration is shown in Figure 3. The value of k is 3.5×10^2 s^{-1} at 300 mg of TiO_2/L. It decreases sharply with TiO_2 concentration attaining a value of 6 s^{-1} at 150 mg of TiO_2/L. Values of k_7 at 100 and 50 mg of TiO_2/RuO_2 are 4 and 1.1 s^{-1}, respectively.

To discuss these observations, we first address the question through which mechanism colloidal RuO_2 mediates water oxidation by $Ru(bpy)_3^{3+}$. Of great significance in this context is the experimental finding that the decay of the $Ru(bpy)_3^{3+}$ absorbance and the increase in conductivity occur always concomitantly. One infers from this observation that the transfer of a positive charge (hole) from $Ru(bpy)_3^{3+}$ to the RuO_2 particle and the release of a proton from water are simultaneous events. This result is by no means trivial since it could be envisaged that the RuO_2 particle after being charged by $Ru(bpy)_3^{3+}$ would store holes for a significant amount of time before water oxidation is effected.[15] In this case the decay of the $Ru(bpy)_3^{3+}$ absorption would not reflect the rate of oxygen generation from water but merely the rate of charging the RuO_2 colloid. Only on the basis of our present combined optical and conductance analysis can such a possibility be ruled out. Thus, the present investigation provides direct evidence for the correctness of the microelectrode concept evoked earlier to rationalize redox catalysis by RuO_2.[16] The particle functions as a local element: holes transferred from $Ru(bpy)_3^{3+}$ to the RuO_2 deposit on TiO_2 are immediately passed on to water, affording oxygen and protons. Under stationary conditions the anodic and cathodic current components are equal and define the overall reaction rate.[17]

Rate limiting under our experimental conditions appears to be the diffusional encounter between the oxidized sensitizer and the catalyst. With a hydrodynamic radius of 200 Å and a density of 3.9 g/cm^3 for the TiO_2 carrier, the concentration of catalyst particles is evaluated as 7×10^{-9} M at 300 mg of TiO_2/L. At this catalyst concentration the specific rate for water oxidation was 3.5×10^2 s^{-1} which would give a true second-order rate constant of 5×10^{10} M^{-1} s^{-1}. This approaches the value of a diffusion-limited rate which from the Smoluchowski–Einstein equation is predicted[18] to be 8.5×10^{10} M^{-1} s^{-1}.

Thus one would conclude that provided the RuO_2 loading is sufficient (≥2%), every encounter of $Ru(bpy)_3^{3+}$ with TiO_2/RuO_2 particles leads to charge transfer and water oxidation. This appears to be the case, however, only at high enough pH. Below pH 5.6 there is a linear dependence of k_7 on OH^- concentration. This could indicate that the species being oxidized is OH^- and not H_2O. Water oxidation seems to become prominent only below pH 4 which would explain the leveling off of the k_7 values in this domain.

In interpreting pH effects, one has to take into account also changes in the surface charge of the TiO_2/RuO_2 particles whose point of zero-zeta potential has been determined as 3.2. Upon lowering of the pH the surface charge will decrease, reducing the rate of $Ru(bpy)_3^{3+}$ encounter with the particle. This could provide an alternative explanation for the finding that the rate of water oxidation decreases with pH.

The effect of TiO_2/RuO_2 concentration on k_7 (Figure 3) indicates that there are significant deviations from simple pseudo-first-order behavior. Doubling the TiO_2/RuO_2 concentration from 150 to 300 mg/L increases the rate of water oxidation ca. 50 times. Similar observations have been made during the study of hydrogen generation from reduced viologens and water in the presence of gold[19] or platinum[20] sols. Two explanations can be offered for this seemingly unusual behavior. As the number of $Ru(bpy)_3^{3+}$ ions produced by the laser pulse is more than 10^3 times higher than that of the TiO_2/RuO_2 particles, blockage of active sites may occur at low catalyst concentration, resulting in restriction of the reaction rate. Secondly, the stability of the TiO_2 sol may be affected by the high $Ru(bpy)_3^{3+}$ concentrations produced in the laser experiments. According to the Schulze–Hardy rule, $Ru(bpy)_3^{3+}$ is a much stronger flocculating agent than the 2+ state. Thus, coagulation of the colloidal catalyst could occur once the number of $Ru(bpy)_3^{3+}$ ions per TiO_2 particle exceeds a critical value.[21] This would also reduce the reaction rate.

---

(15) A. Henglein and J. Little, *J. Am. Chem. Soc.*, **103**, 1059 (1981).

(16) See ref 4c and M. Grätzel, "Faraday Discussions on Photoelectrochemistry", Oxford, U.K., 1980, p 1480.

(17) (a) J. Kiwi and M. Grätzel, *Nature (London)*, **281**, 657 (1979); (b) C. Wagner and W. Traud, *Z. Electrochem.*, **44**, 391 (1938); (c) M. Spiro and A. B. Ravno, *J. Chem. Soc.*, 38 (1965); (d) M. Spiro, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1507 (1979); (e) D. S. Miller, A. J. Bard, G. McLendon, and J. Ferguson, *J. Am. Chem. Soc.* **1981**, *103*, 5336.

(18) This limit for the rate constant does not take into account the Debye correction for charge effects. As the TiO_2 particles are negatively charged in the domain of pH investigated, the rate of reaction with $Ru(bpy)_3^{3+}$ could be even higher.

(19) D. Meisel, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, **85**, 179 (1981).

(20) J. Kiwi and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 7214 (1979).

In both cases deviations from a simple exponential time law are expected both for the decay of $Ru(bpy)_3^{3+}$ and the formation of H^+. Indeed at lower catalyst concentration the kinetic events appear to be biphasic, an initial fast period being followed by a slower component.[22] Only a single exponential is observed at TiO_2/RuO_2 concentrations of at least 200 mg/L.

Conclusion

The present study illustrates the advantage of coupling flash photolytic absorbance and conductance techniques for the study of water decomposition processes. The combination of these techniques proved to be a powerful tool to probe mechanistic details of light-induced oxygen generation mediated by colloidal redox catalysts. Application to the investigation of hydrogen generation is straightforward and presently undertaken.

The extraordinary high activity of colloidal TiO_2 particles charged with ultrafine deposits of RuO_2 has been unequivocally demonstrated. At relatively small RuO_2 concentrations rates for oxygen evolution are in the submillisecond time domain. Such a performance is required in cyclic water decomposition systems. It is comparable to the rate of water oxidation by the water splitting enzyme in photosystem II. However, in the latter case, the mechanism operative consists in the storage of redox equivalents after flash excitation. Only upon repeated exposure to light flashes are protons and oxygen liberated. This contrasts to the mode of intervention of the RuO_2 particles where charging and discharging occur simultaneously. This catalyst is presently being further improved to increase its efficiency in cyclic water decomposition systems.

Acknowledgment. This work was supported by the Swiss National Science Foundation, Ciba Geigy, and the United States Army Procurement Agency Europe.

Registry No. TiO_2, 13463-67-7; RuO_2, 12036-10-1; H_2O, 7732-18-5; O_2, 7782-44-7; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $S_2O_8^{2-}$, 15092-81-6.

---

[21] Pulse radiolysis studies in our institute have shown that Pt sols can be precipitated by reduced viologens (V^+) at high V^+/Pt ratios.

[22] The slower component was used to evaluate k_7. In support of our explanation for the unusual dependenc of k_7 on the catalyst concentration, we found that the value of k_7 increases when the initial $Ru(bpy)_3^{3+}$ concentration produced by the laser pulse was decreased. Thus at 150 mg of TiO_2/L (2% of RuO_2) and $Ru(bpy)_3^{3+} = 2.5 \times 10^{-6}$ M the k_7 value is 4 times larger than with $Ru(bpy)_3^{3+} = 3.6 \times 10^{-6}$ M.

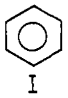
Temporary Anion States of Phosphabenzene, Arsabenzene, and Stibabenzene. Trends in the π and π^* Orbital Energies

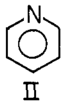
P. D. Burrow,* A. J. Ashe, III,* D. J. Bellville, and K. D. Jordan*,†

Contribution from the Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, and Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennylsvania 15260. *Received February 27, 1981*

Abstract: Electron transmission spectroscopy is employed to study temporary negative ion formation in phosphabenzene, arsabenzene, and stibabenzene in the gas phase. From such measurements, we derive the electron affinities associated with the unstable anionic states of these molecules. The trends in the π^* electron affinities, including previously measured values for benzene and pyridine, are compared with those in the ionization potentials, and interpreted in light of the variations in carbon–heteroatom bond lengths and heteroatom electronegativities. The ground anionic states of the title compounds are found to be stable and thus inaccessible by electron impact. Estimates for the energies of these states are made based on the measured trends in the EA's and IP's. Anion states in addition to those associated with occupation of the π^* orbitals are also observed and possible designations are discussed.

The group 5 heterobenzenes, pyridine (II), phosphabenzene[1] (III), arsabenzene[1] (IV), stibabenzene[2a] (V), and bismabenzene[2b] (VI) form a unique series in which elements down an entire column of the periodic table have been incorporated into aromatic rings. Trends in the energy levels of such a series of closely related compounds can frequently be correlated with the systematic variation of molecular properties. A variety of techniques, both spectroscopic and chemical, have been employed in such studies. Photoelectron spectroscopy, in particular, has been used to determine the ionization potentials (IP's), which may be correlated with the energies of the occupied molecular orbitals, within the context of the Koopmans' theorem approximation.

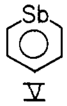

I



II

III

IV



V

VI

Data relating to the normally unfilled orbitals are equally desirable. The frontier molecular orbital theories of chemical reactivity, for example, utilize the energies of the lowest unoccupied molecular orbitals as well as those of the highest occupied molecular orbitals. Invoking Koopmans' theorem again, the energies of the unfilled orbitals can be associated with the measured electron affinities (EA's). In the gas phase, all of the anion states of I and II lie energetically above the ground state of the neutral molecule. Once formed, these temporary anion states undergo electron detachment in times typically of 10^{-13}–10^{-15} s. With the advent of electron scattering techniques, particularly electron transmission spectroscopy[3] (ETS), methods are now available for the study of such anion states. Using ETS, temporary anions are observed as sharp variations in the total scattering cross section as a function of electron impact energy. From such data the electron affinity may be determined, as well as information re-

---

* Address correspondence as follows: University of Nebraska, P.D.B.; University of Michigan, A.J.A. and D.J.B.; University of Pittsburgh, K.D.J.

† Camille and Henry Dreyfus Teacher–Scholar.

[1] Ashe, A. J. III *J. Am. Chem. Soc.* **1971**, *93*, 3293.

[2] (a) Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 6690. (b) Ashe, A. J., III; Gordon, M. D. *Ibid.* **1972**, *94*, 7596. Ashe, A. J., III *Tetrahedron Lett.* **1976**, 415.

[3] Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1972**, *5*, 1672.

0002-7863/82/1504-0425$01.25/0 © 1982 American Chemical Society