hexane, 3:3:2) were magnetically stirred under nitrogen. Product analysis was by gas chromatography using appropriate internal standards.
(6) Only traces of cyclohexene were observed. 1-Halocyclohexenes are partially converted to unknown products under these reaction conditions. Nevertheless the observed high (83-88%) 1-halocyclohexene yields indicate that product instability is not a serious problem.
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Jong Gun Lee, Richard A. Bartsch*
Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

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Relatively Low-Temperature Thermochemical Generation of Molecular Hydrogen from Decomposition of Water by Platinum. Red-Light Photochemical Origin of the Chlorophyll a Water Splitting Reaction

Sir:

The concept of free-energy storage in solar conversion has in recent years focused on the cleavage of water

$$2H_2O \rightarrow 2H_2 + O_2 \quad \Delta G° = 56.7 \text{ kcal/mol} \qquad (1)$$

by heat[1,2] and by visible light.[3,4] The thermochemical generation of hydrogen from water cleavage is limited by the temperature and product removal requirements of reaction 1.[1,2] It is known that Pt is oxidized to yield hydroxides and oxides in the presence of air and water.[5,6] In earlier studies workers investigated[6] the corrosion of Pt in the presence of O_2 and H_2O at ordinary temperatures, and reported that no H_2 was evolved.[6a] However, it was unclear whether hydrogen would be evolved from the thermochemical reaction of Pt with H_2O, in the absence of O_2, at temperatures comparatively lower than those required for the thermal cleavage of water in reaction 1.[1,2] In this communication we describe experiments that delineate the effects of heat and visible light on Pt in deoxygenated water. We report the observation of hydrogen evolution when Pt and water were heated at relatively low temperatures in the range of 130-210 °C. In sharp contrast with the water photolysis results we obtained on illuminating platinized Chl a,[4] no significant amounts of oxygen were detected in the thermochemical Pt-H_2O reaction. No molecular hydrogen and oxygen were detected when Pt in water was illuminated in the visible wavelength region.

Shiny Pt foils were cleaned in aqua regia and flamed over a methane-oxygen torch. Platinization of Pt was accomplished by passing a 30-mA current for 15 min through a 7×10^{-2} M chloroplatinic acid solution containing 6×10^{-4} M lead acetate. The platinized foil was rinsed with distilled water and inserted in a Pyrex cell containing doubly distilled water deoxygenated with Ar gas for 30 min. The sample cell consisted of two sections connected by O-ring joints. Each section was made of 10-mm (o.d.) glass tubing, the lower one being constructed with a glass frit on which the sample was placed, and through which the Ar gas was passed during the degassing of the water. A Kontes 4-mm Kel-F high-vacuum valve was attached to the lower and upper end of the cell assembly to maintain the gas tightness of the system. For application in gas chromatographic analyses, the extreme upper tip of the cell was fitted with another O-ring joint to an evacuation chamber enclosed by a rubber septum through which the gaseous sample was withdrawn into a 100-μL Anspec Pressure-Lok syringe for transfer into a Carle 8700 basic gas chromatograph equipped with a dual thermistor detector and a 2.4-m 80/100 mesh molecular sieve 5A column activated at 300 °C for 4 h in an He gas stream. Argon was used as the sample carrier gas. In mass spectrometric work, the cell was assembled with a ground-glass joint at its upper tip to allow direct attachment to the gas inlet chamber of the mass spectrometer. In light experiments the Pt electrode was irradiated with 4-W, all lines, from a Coherent Radiation Model 53 CW Argon ion laser or with the entire output of a 1000-W tungsten-halogen lamp. In thermal reactions the Pt-H_2O assembly was heated at temperatures up to 210 °C. The mass spectrometric measurements were made using a Consolidated Electrodynamics Corp. 21-110-B mass spectrometer. In the Hersch method[7] for detecting H_2 and O_2, the evolved H_2 gas is determined by burning the hydrogen in a stream of oxygen carried by gaseous He. The level of background O_2 in the He flow was registered as a current amplified by a Keithley 427 current amplifier using the Hersch O_2 indicator constructed in this laboratory.

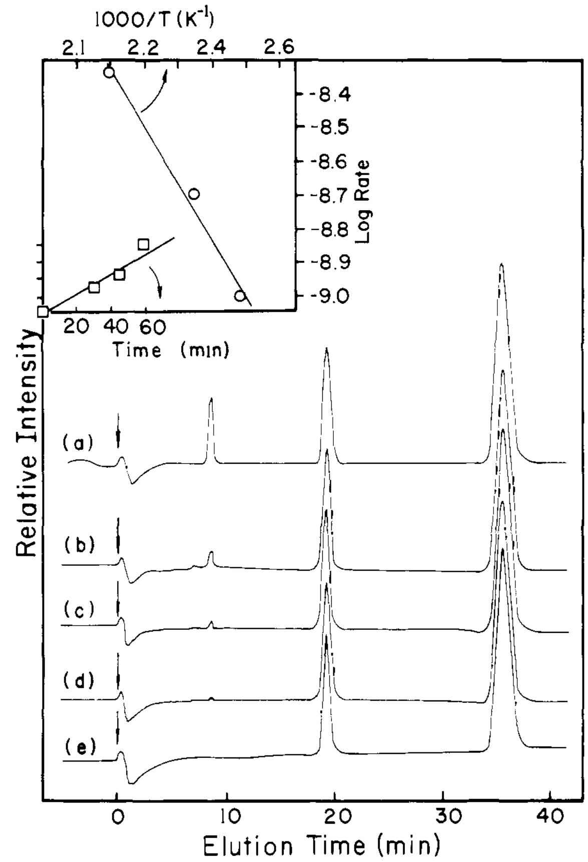

Figure 1. Gas chromatographic determination of hydrogen evolution in the Pt-H_2O reaction: (a) generation of 8×10^{-8} mol of H_2 by passing a 4-mA current for 4 s; (b-d) H_2 generated by heating doubly distilled water at 205 °C in the presence of a platinized Pt foil ($0.8 \times 1.2 \times 0.02$ cm^3) for 60, 45, and 30 min, respectively; (e) gas chromatogram of sample after 1-h irradiation with Ar ion laser. The arrows indicate the time of sample introduction into the gas chromatograph. The position of the hydrogen peak in a provides definitive evidence for the presence of H_2 from the Pt-H_2O reaction. The electrolysis experiment also permits sample calibration. Air leakage through the rubber septum in the evacuation bulb during sample transfer was responsible for the oxygen and nitrogen peaks at 19 and 35 min, respectively. The temperature and time dependences of the hydrogen evolution rate is shown in the inset. The time dependence data points correspond to b-d. The points in the Arrhenius plot were obtained at 205, 155, and 130 °C. The slope of this plot yields an activation energy of 3.48 kcal mol^{-1}.

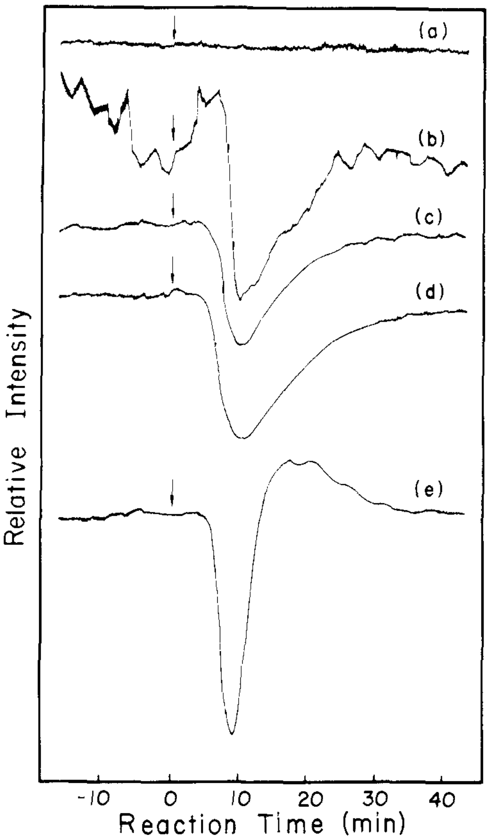

Figure 2. Pyrolytic analyses of hydrogen generated from the Pt–H_2O reaction: (a) doubly distilled water in the absence of Pt; (b) doubly distilled water heated at 130 °C for 30 min in the presence of Pt; (c) pH 11 borax/NaOH buffer illuminated with a 1000-W tungsten–halogen lamp for 30 min in the presence of Pt; (d) pH 9.5 borax/NaOH buffer illuminated as in c in the presence of Pt; (e) H_2 and O_2 generated by passing a 10-mA current for 35 s. The arrows indicate the time of sample introduction into the Hersch analyzer. The samples after the light or heat treatments were cooled for 10 min prior to analysis. The narrow hydrogen band in e is due to the onset of the oxygen peak which is registered in a direction opposite to the H_2 signal. The lack of any detectable effects due to O_2 in samples b–d indicates that only H_2 was evolved from the Pt–H_2O reaction.

The production of H_2 or O_2 in the sample reaction results, respectively, in a decrease or increase in the O_2 background current level.

Gas chromatographic analyses of three experiments, in which the thermal reaction was carried out for 30, 45, and 60 min at 206 °C are compared in Figure 1 with a corresponding analysis of H_2 produced by electrolysis. From this comparison, we estimate that $\sim 4 \times 10^{-8}$ mol h^{-1} of H_2 was liberated by the Pt-H_2O reaction. No H_2 was detected after the Pt black–water sample was irradiated by the Argon ion laser for 1 h, which indicates that Pt is photochemically inactive in the visible wavelength region. The temperature of the Pt-H_2O sample was $\sim$35 °C under continuous illumination by the Ar ion laser radiation. Pyrolytic analyses (using the Hersch method) of experiments in which Pt was illuminated with the tungsten halogen lamp or heated at 130 °C for 20 min in pure water and in pH 9 and 11 $Na_2B_4O_7$/NaOH buffer solutions are shown in Figure 2. The results show that the broad-band visible–IR light source, capable of heating the Pt-H_2O sample to 150 °C, has effectively produced the same outcome as the heat. From a comparison of these results with corresponding results obtained for H_2 and O_2 generated by electrolysis, it became evident that little O_2 was produced in the Pt-H_2O reaction. From a calibration of the hydrogen evolution in the sample reaction against electrolysis we observed that H_2 was produced at a rate of 2×10^{-6} mol h^{-1}, about two orders of magnitude greater than the production rate measured in the GC study under comparable experimental conditions.[8]

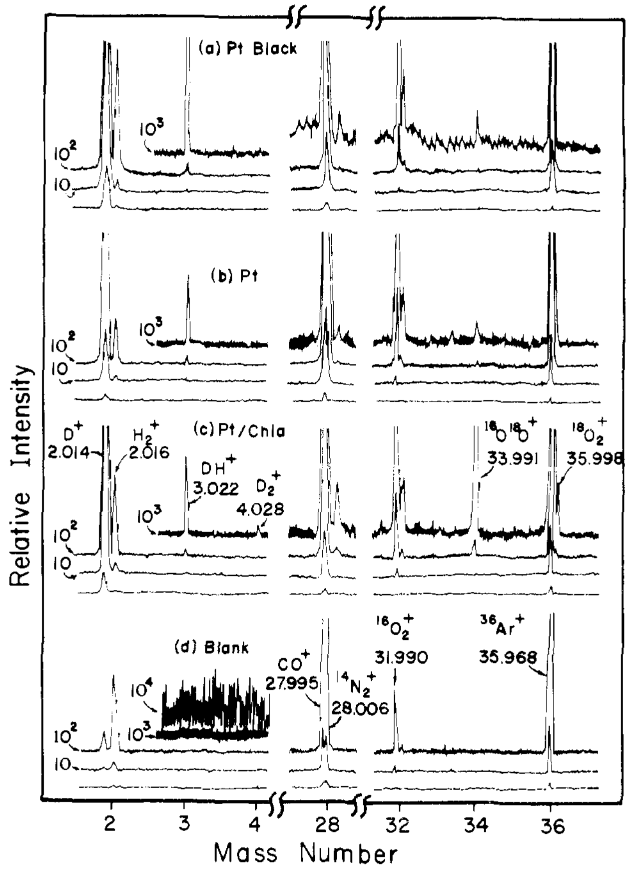

Figure 3. Comparison of the mass spectrometric determination of products from the Pt–H_2O reaction with that of products from the photoelectrolysis of water by platinized Chl a: (a) doubly distilled water heated for 30 min in the presence of Pt black; (b) pH 11 borax/NaOH buffer heated for 30 min in the presence of shiny Pt; (c) platinized Chl a illuminated for 30 min using red light from a 1000-W tungsten–halogen lamp; (d) doubly distilled water heated for 30 min in the absence of Pt. The ratio of the mass 34 ($^{18}O^{16}O^+$) line to the mass 36 ($^{18}O_2^+$) line in c is 37.0, in agreement with the ratio obtained by electrolysis. The mass 2 (D^+) line is attributable, in part at least, to water fragmentation.[4a,15] The H_2^+ line in d may be due to trace amounts of H_2 present in the mass spectrometer. The $^{36}Ar^+$ line was used as an internal standard for calibration. The mass 1 (H^+) line was not observed owing to instrumental limitations. The spectra in the low- and high-mass regions were measured with the spectrometer focused at masses 2 and 40, respectively.

The above observations on the Pt-H_2O reaction were corroborated by a quantitative mass spectrometric analysis of this reaction using a mixture of $D_2{}^{16}O$ and $H_2{}^{18}O$ (H:D ratio, 1:1; ^{16}O:^{18}O ratio, 68.7:31.3) after heating at 130 °C for 30 min. The mass spectra of sample reactions after 30 min of heating at 130 °C are given in Figures 3a and 3b. On calibration against electrolysis we obtained the H_2 evolution rate of 2.7×10^{-6} mol h^{-1}.[8] The results of the Pt-H_2O reaction are compared with those of water photolysis by platinized Chl a[9] in Figure 3c, in which the results shown have been obtained using a 1000-W tungsten–halogen projection lamp with a 10-in. water filter to eliminate heating from the IR radiation and a Corning CS 2-63 cut-off filter to remove photons at wavelengths of λ <580 nm. Also shown is a blank spectrum (Figure 3d) obtained after the isotopic water was heated in the absence of Pt under otherwise identical conditions. The relative line intensities at masses 2 (H_2^+), 3 (HD^+), 4 (D_2^+), 34 ($^{16}O^{18}O^+$), and 36 ($^{18}O_2^+$) observed in the water photolysis experiments (Figure 3c) are in good agreement with the electrolysis experiments.[5] Similar relative line intensities for the various isotopic hydrogen and oxygen molecular ions were observed from water photolysis using (Chl $a{\cdot}2H_2O)_n$ films on microscope slides in the absence of Pt, although the quantum efficiency of water photolysis in this case is nearly two orders of magnitude lower than that corresponding to the results shown in Figure 3c. In contrast, for comparable line intensities at masses 2 (H_2^+), 3 (HD^+), and 4 (D_2^+) obtained in the Pt-H_2O experiments, the intensity of lines at masses 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) are significantly weaker than those observed in the photolysis and electrolysis runs (compare Figures 3b and 3c). The weak mass 34 ($^{16}O^{18}O^+$) line observed in Figures 3a and 3b is greater than that expected from the 0.2% natural abundance of ^{18}O, however, and may be a result of isotopic redistribution of ^{18}O in the water and O_2 present as contamination from the atmosphere. The possibility that this line may have resulted from water decomposition appears rather unlikely from thermodynamic considerations.[10,11]

We rule out H_2O_2 as a product in the Pt-H_2O reaction by mass spectrometric determinations and by the colorimetric triiodide method.[12] Among possible explanations for the experimental effects described above is the thermodynamically characterized reaction[13]

$$2H_2O + Pt \xrightarrow[\Delta]{} Pt(OH)_2 + H_2 \quad \Delta G° = 49.7\ \mathrm{kcal/mol} \qquad (2)$$

in which Pt is oxidized in the reduction of the water. Reaction 2 is uphill in free energy, having an equilibrium constant $K \sim 10^{-27}$ at 150 °C. The observation of H_2 may be rationalized in spite of this unfavorable equilibrium constant on account of the fact that $Pt(OH)_2$ is extremely insoluble in water, so that reaction 2 is expected to occur entirely at the Pt-H_2O interface. The displacement of H_2 from the relatively hot ($\gtrsim$150 °C) reaction zone to the cooler (~40 °C) gaseous space above the water would thus shift the equilibrium of reaction 2 to the right. This interpretation appears to be consistent with the observed temperature dependence of the H_2 evolution rate (see inset, Figure 1). From tables of H_2 solubility[14] we estimate that the enthalpy of H_2 solvation in water at the boiling point of water is 3.62 kcal mol^{-1}. This value is in fair agreement with the activation energy 3.48 kcal mol^{-1} obtained from the Arrhenius plot in Figure 1.

In conclusion we have described the generation of molecular hydrogen in the thermochemical decomposition of water by Pt. In addition we have also established the red-light photochemical origin of the Pt/Chl a water splitting reaction based on the mass spectrometric data in Figure 3.

Acknowledgment. The method of gaseous sample transfer in the GC analysis was suggested by Dr. R. H. Wentorf, Jr.

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(8) The discrepancy between the rate determination from the GC analysis and the determination in mass spectrometric and pyrolytic studies could have originated from variations in the quality of the platinum surface and the extent to which air had been excluded from the sample. More probably, however, the difficulty may be attributable to systematic errors arising from the sample transfer procedure in the GC analysis. The mass spectrometric and Hersch determinations, unlike the GC work, were on-line experiments.

(9) Preparation procedures for the Pt-Chl a sample have been previously described in ref 4.

(10) Patents issued to French workers (*Chem. Abstr.*, **86**, 157711f, 191950t (1977)) described the thermochemical cleavage of water in the temperature range 100–1200 °C using a finely divided Pt group metal, preferably Pd, as catalyst. The H_2 and O_2 were reportedly generated in a chamber, the walls of which were selectively permeable to H_2. According to the present observations it would appear that Pt, being consumed in the Pt-H_2O reaction, would not be a suitable catalyst for reaction under conditions specified by these French workers.

(11) The effect of heat on Pt immersed in water was examined by comparing the rate of the catalytic decomposition of H_2O_2 by a Pt black sample heated in water for 20 h at 180 °C with that by an identically prepared Pt black sample stored in water at room temperature for 20 h. Both electrodes were maintained under an Ar atmosphere during the heat treatments. The rate of H_2O_2 decomposition catalyzed by each sample was subsequently determined by the colorimetric triiodide method.[12] The unheated Pt sample decomposed H_2O_2 at a rate 7.24×10^{-4} mol cm^{-2} s^{-1}, approximately twice that, 4.20×10^{-4} mol cm^{-2} s^{-1}, using the heat treated platinum. The results indicate that the number of Pt active sites was decreased as a result of heating the platinum in water. Details of these results will be published elsewhere.

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L. Galloway, D. R. Fruge, G. M. Haley
A. B. Coddington, F. K. Fong*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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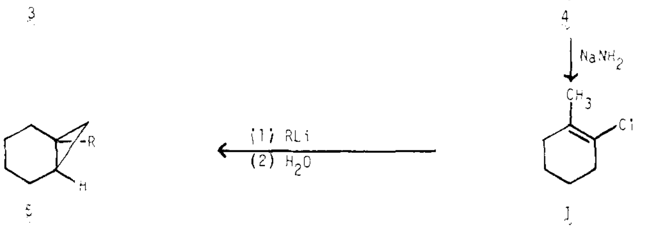
Reactions of 1-Chloro-2-alkylcyclohexenes with Organolithium Reagents. The Intermediacy of Cyclopropenes

Sir:

In 1967, it was reported that a mixture of 1-chloro-2-methylcyclohexene (**1**) and 1-chloro-6-methylcyclohexene (**2**) reacted with phenyllithium to yield 1-phenyl-3-methylcyclohexene, 1-phenyl-6-methylcyclohexene, and unreacted **1**.[1,2] In view of our recent findings on the reactions of vinyl halides with organolithium reagents,[3] the reported poor reactivity of **1** with phenyllithium seemed surprising. Thus, we set out to synthesize pure **1** and to investigate its behavior in the presence of organolithium reagents. We now report that **1** reacts with a variety of organolithium reagents to yield substituted bicyclo[4.1.0]heptanes. Mechanistic studies suggest the intermediacy of the highly strained cyclopropene, bicyclo[4.1.0]heptene-$\Delta^{1,6}$.

Pure **1** was prepared in 41% overall yield from 1-methylcyclohexene (**3**)[4] via the dichloride, **4**, which resulted from the reaction of **3** with iodobenzene dichloride (Scheme I). Dehydrochlorination of **4** with sodium amide in liquid ammonia gave

Scheme I



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