quired to have a much greater acid strengthening effect in its coördination with chromium(VI) than is required of it in its coördination with sulfate, if the 1:1 complex is to be $CeCrO_4^{++}$. It may be argued, however, that hydrogen ion and CrO_3 have a sufficient acid strengthening effect upon $HCrO_4^-$ to make it ionize to a significant extent in a medium of 1 *M* hydrogen ion since the acid dissociation quotients for H_2CrO_4 and $HCr_2O_7^-$ in media of unit ionic strength are 1.21 and 0.85, respectively.[7b] It would not be surprising for Ce^{+4} to, similarly, cause the ionization of the hydrogen ion of $HCrO_4^-$ in a medium of 1 *M* hydrogen ion. The value of *K* (defined earlier) may be converted into a value of the equilibrium quotient for the reaction $Ce^{+4} + CrO_4^= = CeCrO_4^{++}$ if one assumes that the predominant 1:1 complex species is $CeCrO_4^{++}$. The value of the equilibrium quotient for this reaction is 10^{10} (to the nearest power of ten). The value of the analogous equilibrium quotient for the formation of the species $CeSO_4^{++}$ is approximately 10^3 (to the nearest power of ten). It is seen that the cerium(IV)–chromate complex is much more stable than the cerium(IV)–sulfate complex.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Influence of Perchloric Acid and Cerous Perchlorate upon the Photochemical Oxidation of Cerous to Ceric Perchlorate in Dilute Aqueous Perchloric Acid

BY LAWRENCE J. HEIDT AND ALAN F. MCMILLAN[1,2]

RECEIVED NOVEMBER 30, 1953

The quantum yield of the photochemical oxidation of cerous to ceric perchlorate in water by light absorbed by the cerous species has been found to be increased when either the concentration of perchloric acid or cerous perchlorate or both have been increased. The reciprocal of the yield depends linearly upon the reciprocal of either of these concentrations when other variables are held constant. A small linear extrapolation of these relationships reveals that the maximum possible quantum yield of the reaction in this system at 25° with light of 2537 Å. is 0.0014 mole of cerous converted to ceric ions, equivalent to the production of 0.0007 mole hydrogen gas, per mole of light quanta absorbed by the cerous state. A set of reactions has been found which is in quantitative agreement with the data. This set is not necessarily a unique solution to the problem but it is a simple and reasonable solution; simple alternative reactions have been evaluated. Some new evidence has been obtained confirming the production of hydrogen by the light absorbed by the cerous ions. The key intermediate in the reaction appears to be the ion $(H_2O)_5Ce\text{-}OH\text{-}H_2^{+4}$ which reacts with hydrated cerous ions to produce ceric ions and hydrogen. An estimate of the oxidizing power of the hydrogen molecule ion in water shows that its standard oxidizing potential is at least 2.3 v. with respect to reduction to hydrogen compared to about 1.7 v. for ceric reduced to cerous ion so it is not surprising that cerous ions are oxidized to ceric ions in the above reaction.

The photochemical reduction of ceric to cerous ions in dilute aqueous perchloric acid has been known for some time to be accompanied by the evolution of oxygen[3,4] and to be greatly inhibited by cerous ions.[5] The latter effect has been found to be due partly to the inner filter effect of the cerous ions, partly to deactivation of the photon excited ceric ions by the cerous ions and, in so far as the change in the concentration of ceric ions is concerned, partly to the oxidation of cerous to ceric ions by light absorbed by the cerous ions.[6] Evidence has been obtained for the production of hydrogen by the photochemical oxidation of cerous to ceric ions[7] and for the production of both hydrogen and oxygen by the irradiation of a water solution of cerous and ceric perchlorates under certain conditions.[8] It has been recognized,[8] moreover, that since water can be oxidized by ceric perchlorate even in the dark,[9] while its reduction by cerous perchlorate occurs only in light, an aqueous solution containing both ceric and cerous ions can be made to produce alternatively pure oxygen in darkness and almost pure hydrogen in light or both gases simultaneously largely free from each other from separate parts of a solution by an appropriate design of the apparatus.

This article reports for the first time the results of a study of the influence of the concentrations of acid and cerous ions upon the quantum yield of the photochemical oxidation of cerous ions at 25° by light of 2537 Å., and an evaluation based on these results of the maximum possible quantum yield of the reaction in this system and of the nature of the reactions by which water is photochemically reduced by light absorbed by cerous ions. Some additional evidence is presented for the production of hydrogen by the photochemical reduction of water by light absorbed by cerous ions.

(1) We are indebted to the Godfrey L. Cabot Fund of M. I. T. for financial aid in support of this work. This is publication No. 35 of the M. I. T. Solar Energy Conversion Project.

(2) This article is based mostly on material presented in the thesis of Alan F. McMillan in partial fulfillment of the requirements for the Ph.D. degree in Physical Chemistry at M. I. T., September, 1953.

(3) E. Bauer, *Z. physik. Chem.*, **63**, 683 (1908).

(4) An investigation of the photochemical oxidation of water by ceric perchlorate also has been carried out by B. Ya. Dain and A. A. Kachan, *Doklady. Akad. Nauk. S.S.S.R.*, **67**, 85 (1949) in Russian, but see *C. A.*, **43**, 7349 (1949) for a summary of this work in English. Dain and Kachan followed the reaction over the range 6 to 60° by measuring the amount of oxygen evolved when the solution was irradiated with light of 313 mμ. They came to the conclusion that the production of oxygen is the result of a heterogeneous reaction on the surface of the quartz reaction vessel and that there is no production of oxygen in the dark, *i.e.*, by a thermal reaction, unless preceded by the photochemical reaction. They make no mention of any attempt to determine if stirring could be made adequate to eliminate dependence of the quantum yield upon the rate of stirring—a very important aspect of photochemical work when a large part of the actinic light is absorbed by a thin layer of the solution next to the wall of the vessel.

(5) J. Weiss and D. Porret, *Nature*, **139**, 1019 (1937).

(6) L. J. Heidt and M. E. Smith, THIS JOURNAL, **70**, 2476 (1948).

(7) L. J. Heidt, *Proc. Am. Acad. Arts Sci.*, **79**, 228 (1951).

(8) L. J. Heidt and A. F. McMillan, *Science*, **117**, 75 (1953).

(9) D. Klop and H. C. Thomas, THIS JOURNAL, **71**, 3047 (1949).

Experimental

The materials and solutions, the procedures, the actinometry and the analytical chemical methods were essentially the same as previously employed in this Laboratory.[6,8] The chemicals for the most part were of analytical reagent grade. The source of cerium was ceric ammonium nitrate of reference purity. The cerium in this compound was converted in water solution first into the hydroxide to remove ammonia and nitrate, then into a mixture of cerous and ceric perchlorates in perchloric acid and finally by electrolysis into solutions consisting largely of either cerous or ceric perchlorate. The electrolyses were carried out with the platinum gauze electrodes commonly used for the determination of copper. Conductivity water was used for the perchlorate solutions. Care was taken to exclude from the cerium solutions all negative ions except perchlorate, strong light absorbing metallic ions, such as iron, and organic material. Acidity and ionic strength were adjusted by means of perchloric acid and sodium carbonate.

Solutions were irradiated at 25 ± 0.02° with 2537 Å. light over 98% pure and containing no light of shorter wave length. Fluctuations in the intensity of the light falling on the solutions were kept small in the manner previously described[10] and by inserting a 2KVA voltage regulator in the a.c. feed circuit to stabilize the voltage at 115 ± 0.3 v. Intentional changes in the light intensity were brought about by means of a variac in the primary circuit of the transformer feeding directly into the lamp.

The apparatus employed to irradiate the solutions and to identify the gases produced has not been previously described in detail so it is sketched in Fig. 1 since it would have required prohibitively long periods of time to bring about the reaction to a measurable extent with conventional equipment. The volume of the reaction mixture was 30 ml. in every case. The intensity of the light falling on the solution was measured four times during the course of an experiment, at the beginning, at the end and twice at nearly equal intervals in between. This was done by means of a uranyl oxalate actinometer 0.0102 *M* in uranyl oxalate and 0.014 *M* in oxalic acid. The decomposition of the oxalate was held to less than 25%.

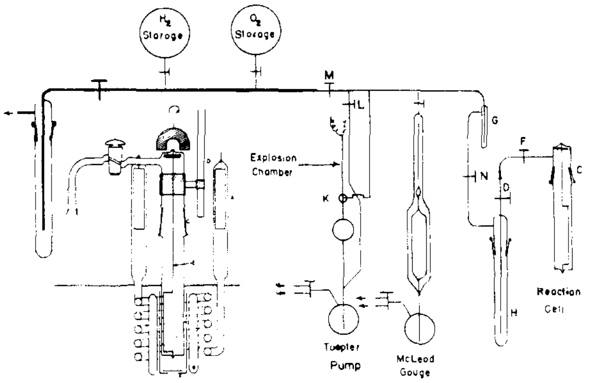

Fig. 1.—Apparatus employed to irradiate the solutions and to identify the composition of the gas produced. The solution in the clear fused quartz reaction vessel (2.8 cm. o.d.) attached to C (a standard tapered joint 34/45) was stirred by means of the bent glass rod which was rotated by a magnet appropriately placed outside the reaction vessel. The reaction vessel was always placed so that the solution was irradiated when centered with respect to the space enclosed by the filter, B, and the source of light in the lamp coil surrounding this filter. The position of the reaction vessel relative to C and the rod (not the stopcock) D was fixed by aligning a mark on the reaction vessel with a mark on C. Copper metal foil was wrapped around the vertical arms of the lamp to eliminate stray light and to conduct heat away to the water-bath.

The small concentrations of ceric perchlorate produced by the photoxidation of the cerous ions were determined spectrophotometrically without removing the solutions from the reaction vessel. This was done by measuring the optical density with a beam of light having a band width of 3 Å. centered at 3500 Å. A Cary Spectrophotometer was employed for this purpose. The reaction vessel was placed in water in the cell compartment of the spectrophotometer in such a way that the position of the reaction vessel was easily reproduced. This was done by fastening to the spectrophotometer a boss which fitted snugly into a hole drilled into the rod D sketched in Fig. 1. The path of the beam of 3500 Å. light through the solution in the reaction vessel was 2.60 cm. when the beam was cut down to a width of 0.95 cm. Care was taken to keep the stirring rod in the reaction vessel clear of this beam.

Variations in the average molar extinction coefficient at 3500 Å. of the ceric species, *i.e.*, variations in $E = \log (I_0/I)/cd$ where c represents gram atoms of ceric cerium per liter and d is expressed in cm., were noted in solutions 1×10^{-4} to 20×10^{-4} *M* in ceric ions containing also 0 to 0.5 *M* cerous ions and 0.1 to 1.1 *M* perchloric acid at ionic strengths between 1 and 3 *M*. Only the ceric ions absorbed a measurable fraction of the light. The variations in E ranged from 700 to 800 and could be explained by assuming equilibria between hydrated monomeric ceric ions such as $CeOH^{+3}$ and $Ce(OH)_2^{+2}$, and dimers of these species such as $Ce\text{-}O\text{-}Ce^{+6}$, etc., if at this wave length a molar extinction coefficient of 700 is ascribed to all the monomeric species and of 1700 to all the dimeric species and the formation constants of these species equal the values obtained in this Laboratory from e.m.f. and quantum yield measurements.[11]

The vacuum system employed to degas the solutions and to identify and measure the gases produced in them is outlined in Fig. 1. The Toepler pump, explosion chamber and the manner in which they were operated are described in detail elsewhere.[8] The stopcocks and joints were lubricated with apiezon vacuum stopcock grease which was used sparingly and kept out of the other parts of the system. Gas measurements were made only when the system held a vacuum of at least 10^{-5} mm. for several hours and of 10^{-4} mm. overnight. The cold traps including G in Fig. 1 were refrigerated with liquid nitrogen.

Results

Part I. Additional Experimental Evidence for the Production of Hydrogen by the Photochemical Reduction of Water by Light Absorbed by Cerous Ions.—The new evidence we have obtained for the production of hydrogen by the photoxidation of cerous to ceric ions in dilute perchloric acid is of the following kind. A water solution was made up containing initially per liter about one mole perchloric acid, 0.06 mole cerous perchlorate and no other ingredients; it was then irradiated under its own vapor pressure at 25° with about 0.01 einstein of light of 2537 Å. About 5×10^{-8} mole of the evolved gas was passed slowly through a cold trap

---

[10] L. J. Heidt and H. B. Boyles, THIS JOURNAL, **72**, 5728 (1951).

[11] The ceric monomers in these solutions were assumed to be only the hydrated species of $CeOH^{+3}$ and $Ce(OH)_2^{+2}$. A value of 0.6 was taken for the equilibrium constant of the reaction $CeOH^{+3} + H_2O = Ce(OH)_2^{+2} + H^+$. This value was obtained from e.m.f. measurements by M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943). The formation constants of the dimers were taken as 50, 50 and 100 for the reactions $2CeOH^{+3} = Ce\text{-}O\text{-}Ce^{+6} + H_2O$, $2Ce(OH)_2^{+2} = HOCe\text{-}O\text{-}CeOH^{+4}$ and $CeOH^{+3} + Ce(OH)_2^{+2} = Ce\text{-}O\text{-}CeOH^{+5} + H_2O$, respectively. These reactions were postulated and their equilibrium constants were evaluated from quantum yield and e.m.f. measurements by L. J. Heidt and M. E. Smith.[6] Some additional evidence has been obtained more recently for the existence of ceric dimers from the kinetics of the thermal reduction of ceric to cerous perchlorate in water by D. Klop and H. C. Thomas[9] and from spectrophotometric measurements carried out in the visible and near ultraviolet by T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951), and by E. L. King and M. L. Pandow, THIS JOURNAL, **74**, 1966 (1952). Our optical density measurements at 3500 Å. were not extensive enough to determine unequivocally whether or not the molar extinction coefficients of the different ceric species, especially the monomeric species, are identical or even closely similar at this wave length.

immersed in liquid nitrogen, and subsequently collected under a pressure of about 30 mm. in the explosion chamber. The gas was then ignited with a spark whereupon the amount of gas in the chamber at room temperature and still under a pressure of 30 mm. was found to have been decreased by 0.5 × 10^{-8} mole. The gaseous residue in the explosion chamber then was mixed with excess oxygen and ignited with a spark whereupon the amount of gas in the chamber was found to have been decreased by an amount corresponding to the complete formation of water vapor by the gaseous residue of the initial explosion. The amount of ceric ions produced by photolysis in this experiment was found to be 1.3 × 10^{-5} mole, so most of the hydrogen presumably produced by the reaction was left behind in the reaction vessel and cold traps.

The previously published evidence for the production of hydrogen by the reaction is of two kinds: one kind[7] consists of having noted that a copper mirror was produced when the gas evolved by the reaction was passed slowly over hot black cupric oxide after the gas had been passed slowly through a cold trap immersed in liquid nitrogen, the other kind[8] consists of evidence similar to the kind described here except that both hydrogen and oxygen were found to be produced in more nearly equivalent amounts by the irradiation of mixtures containing initially both cerous and ceric perchlorates in dilute perchloric acid.

Part II. The Influence of Perchloric Acid and Cerous Perchlorate upon the Photochemical Efficiency of the Oxidation of Cerous to Ceric Perchlorate.—The influence of variations in the concentrations of perchloric acid and cerous perchlorate upon the quantum yield, ϕ^*, for the conversion of cerous to ceric perchlorate by light of 2537 Å. absorbed by the cerous perchlorate was determined by measuring the increase in the concentration of ceric perchlorate upon irradiation with this light of solutions in which all of the cerium was initially in the cerous state. Some typical results are illustrated in Fig. 2. It will be noted that the initial increase in the concentration of ceric perchlorate depends linearly upon the amount of light absorbed by the system, but in some cases falls off as the ceric ions accumulate as illustrated in Fig. 2 at the lowest initial concentration of cerous ions. This falling off in the rate of increase in the concentration of ceric perchlorate can be attributed to the inner filter effect of the ceric ions, also to the reduction of ceric to cerous ions when the concentration of ceric ions becomes large enough for ceric dimers to absorb a significant fraction of the light.[6] The initial slope of any of the lines in Fig. 2 equals ϕ^* in the absence of any ceric perchlorate.

The effect of air upon the photochemical conversion of cerous to ceric ions was found to be negligible since the slopes of lines like those in Fig. 2 were the same when air was intentionally or accidentally admitted to the system. The half filled circle on the middle line of Fig. 3 represents the results of an experiment performed in the absence of air. The other points in Fig. 3 represent results obtained in the presence of air at atmospheric pressure. Changes in the rate of stirring and in the light intensity over ranges of about fivefold had no observable effect upon the reaction.

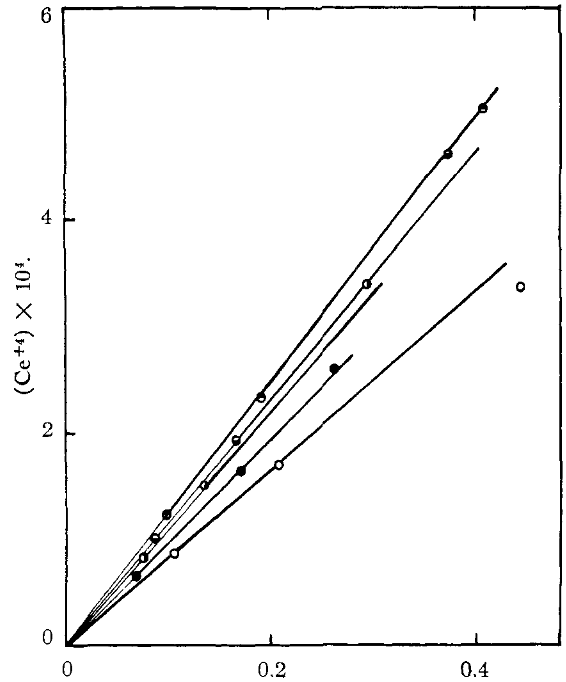

Fig. 2.—Typical increases in the formal concentration of ceric perchlorate, (Ce^{IV}), brought about at 25° by light of 2537 Å. absorbed by solutions 1.03 M in perchloric acid and containing initially all of the cerium in the cerous state. The values are on a liter basis. The results in descending order were obtained at progressively lower concentrations of cerous perchlorate ranging from 0.064 to 0.0041 mole per liter all at an ionic strength of 1.42.

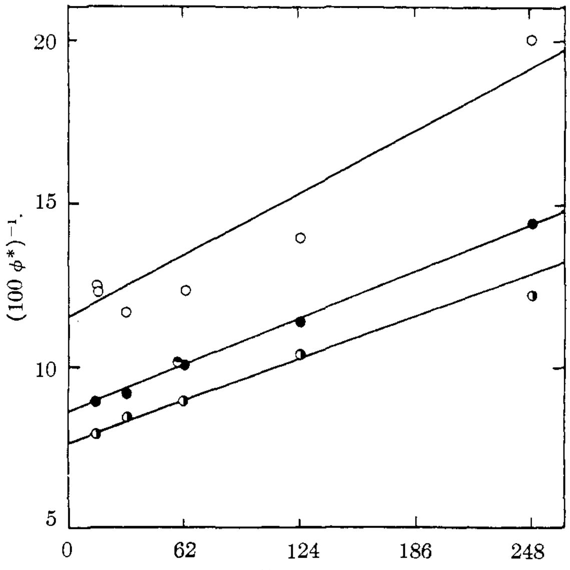

Fig. 3.—Influence of cerous ions, Ce^{+3}, upon the quantum yield, ϕ^*, for the conversion of cerous to ceric ions by light absorbed only by cerous ions at three levels of the concentration of perchloric acid, namely, at 0.114, 0.343 and 1.03 M in descending order all at 25° and an ionic strength of 1.42.

The results presented in Fig. 3 show that ϕ^* increases with increase in the concentration of cerous ions, (Ce^{+3}), at three different levels of the concentration of acid and that ϕ^* is increased also by increasing the concentration of acid since the lines representing progressively higher acid concentrations fall at progressively lower values of $1/\phi^*$.[12]

The dependence of ϕ^* upon the concentration of acid is shown by the upper line in Fig. 4 where the values of $1/\phi^*$ obtained by extrapolating the straight lines in Fig. 3 to $1/(Ce^{+3})$ equal to zero are plotted against $1/(H^+)$. Extrapolation of the upper line in Fig. 4 to $(H^+) = \infty$ and $(Ce^{+3}) = \infty$ gives the maximum quantum yield of the reaction at 25°. This value is 1/700 or 0.0014 or 0.14% for the conversion of cerous to ceric ions and this is equivalent to 0.0007 mole hydrogen gas per mole of light quanta of 2537 Å. absorbed by the cerous ions in this system at 25°.

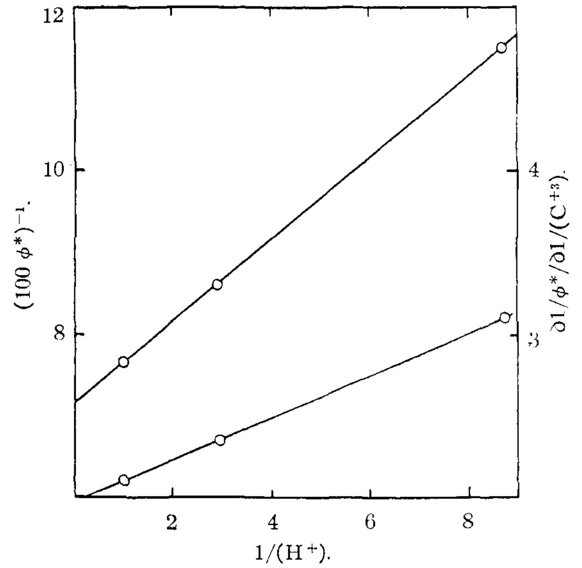

Fig. 4.—Influence of acid upon the quantum yield, ϕ^*, as obtained in the case of the upper line from the values of the intercepts and in the case of the lower line from the slopes of the lines in Fig. 3. The maximum possible value of the quantum yield of the reaction in these solutions is obtained from the value of the upper line in this figure when $1/(H^+)$ equals zero.

Discussion

The following set of reactions accounts quantitatively for the influence of variations in the concentrations of perchloric acid and cerous perchlorate upon the quantum yield, ϕ^*.

Forward Reactions:

$$Ce\cdot H_2O^{+3} + h\nu = {}^*Ce\cdot H_2O^{+3} \quad (1)$$

$$^*Ce\cdot H_2O^{+3} + H_3O^+ = Ce\text{–}OH\text{–}H_2^{+4} + H_2O \quad (2)$$

$$Ce\text{-}OH\text{-}H_2^{+4} + Ce\cdot H_2O^{+3} = 2CeOH^{+3} + H_2 + H^+ \quad (3)$$

The sum of reactions 1, 2 and 3 is $2Ce\cdot H_2O^{+3} + h\nu = 2CeOH^{+3} + H_2$

Quenching Reactions:

$$^*Ce\cdot H_2O^{+3} = Ce\cdot H_2O^{+3} + \text{heat} \quad (1')$$

$$^*Ce\cdot H_2O^{+3} + H_3O^+ = Ce\cdot H_2O^{+3} + H_3O^+ + \text{heat} \quad (2')$$

$$Ce\text{-}OH\text{–}H_2^{+4} + H_2O = Ce\cdot H_2O^{+3} + H_3O^+ + \text{heat} \quad (3')$$

The meaning of the symbols in these equations is: $Ce\cdot H_2O^{+3}$ or Ce^{+3} represents hydrated cerous ions, namely, $(H_2O)_5Ce^{+3}\cdot H_2O$; $Ce\text{–}OH\text{–}H_2^{+4}$ represents $(H_2O)_5Ce^{+4}\text{–}OH^-\text{–}H_2^+$; $^*Ce\cdot H_2O^{+3}$ represents photon activated $Ce\cdot H_2O^{+3}$; $CeOH^{+3}$ represents $(H_2O)_5CeOH^{+3}$; H^+, H_3O^+ or $H^+ + H_2O$ represents the hydrated proton.

The above reactions give the following mathematical relationships between ϕ^* and the components of the system:

I. $\phi^* = d(Ce^{IV})/Idt = 2k_3(Ce\text{–}OH\text{–}H_2^{+4})(Ce^{+3})/I$ where I represents light absorbed by cerous ions per unit time per unit volume.

II. $d(^*Ce^{+3}\cdot H_2O)/dt = I = k_2(^*Ce^{+3}\cdot H_2O)(H^+) + k_1'(^*Ce^{+3}\cdot H_2O) + k'_2(^*Ce^{+3}\cdot H_2O)(H^+) = -d(^*Ce^{+3}\cdot H_2O)/dt$; hence $(^*Ce^{+3}\cdot H_2O) = I/[k_1' + (k_2 + k_2')(H^+)]_1$.

III. $d(Ce\text{–}OH\text{–}H_2^{+4})/dt = k_2(^*Ce^{+3}\cdot H_2O)(H^+) = k_3(Ce\text{–}OH\text{–}H_2^{+4})(Ce^{+3}) + k_3'(Ce\text{–}OH\text{–}H_2^{+4}) = -d(Ce\text{–}OH\text{–}H_2^{+4})/dt$; hence $(Ce\text{–}OH\text{–}H_2^{+4}) = (^*Ce^{+3}\cdot H_2O)k_2(H^+)/[k_3' + k_3(Ce^{+3})]_2 = Ik_2(H^+)/[\ ]_1[\ ]_2$.

Therefore, $1/\phi^* = a + b/(Ce^{+3}) + c/(H^+) + d/(H^+)(Ce^{+3})$; where $a = (k_2 + k_2')/2k_2$, $b = ak_3'/k_3$, $c = k_1'/2k_2$ and $d = ck_3'/k_3$. The k's represent the rate constants for the respective reactions.

Reaction 1 represents the fact that the reaction is initiated by light absorbed by cerous ions.

Reactions 2 and 1′ account for the observed dependence of $1/\phi^*$ and upon $1/(H^+)$. The terms containing (H^+) would be negligible if reaction 2 took place but reaction 1′ and consequently k_1' were negligible.

Reactions 3 and 3′ account for the observed dependence of $1/\phi^*$ upon $1/(Ce^{+3})$. The terms containing (Ce^{+3}) would be negligible if reaction 3 took place but reaction 3′ and consequently k_3' were negligible.

Reaction 2′ accounts for the fact that $1/\phi^*$ does not equal $^1/_2$ by extrapolation when both $1/(H^+)$ and $1/(Ce^{+3})$ equal zero. The constant a would equal $^1/_2$ if reaction 2′ and consequently k_2' were negligible.

The values of the constants a and c are obtained from the plot of $1/\phi^*$ *vs.* $1/(H^+)$ when $1/(Ce^{+3})$ equals zero, *i.e.*, from the upper line in Fig. 4. The value of the intercept of this plot on the $1/\phi^*$ axis equals $700 = a = {}^1/_2 + k_2'/2k_2$; hence k_2'/k_2 equals 1400 very nearly and the reaction between photon activated cerous ions and hydrated protons leads fourteen hundred times more often to the dissipation of the energy of the absorbed photon as heat

---

[12] These results may erroneously suggest that the decrease in ϕ^* with decreasing concentration of cerous perchlorate can be attributed to the inner filter effect of the ceric ion and to the photochemical back reaction of ceric to cerous perchlorate since the ratio of ceric produced to cerous remaining increases as the initial concentration of cerous perchlorate was decreased. Considerations of this kind, however, fall far short of accounting for all of the decrease in ϕ^* with decrease in the initial concentration of cerous ions because the inner filter effect at 2537 Å. of the ceric ions in any of our solutions is only a small fraction of the observed decrease in ϕ^* (the extinction coefficients of ceric and cerous perchlorates at 2537 Å. are given in the earlier work[6]) and because the quantum yield for the conversion of ceric to cerous ions is close to zero when the ratio of the concentration of cerous to ceric ions is high or the concentration of ceric ions is low, the former because of the inhibiting effect of cerous ions upon the conversion of ceric to cerous ions and the latter because of the decrease in the concentration of the photo-sensitive ceric dimers.[6]

than to the propagation of the measured reaction. The slope of this plot equals $50 = c = k'_1/2k_2$; hence k'_1/k_2 equals 100 and $a/c = 14 = k'_2/k'_1$ very nearly so hydrated protons are about fourteen times more effective than all other species in quenching the measured reaction when the concentration of perchloric acid is one molar and all other solutes are absent except cerous perchlorate.

The values of the constants b and d are obtained from the plot of $\partial(1/\phi^*)/\partial[1/(\mathrm{Ce}^{+3})]$ *vs.* $1/(\mathrm{H}^+)$, *i.e.*, from the lower line in Fig. 4. The constant b equals 2 from the value of this line when $1/(\mathrm{H}^+)$ equals zero and the constant d equals 0.13 from the slope of this line. Since $b = ak'_3/k_3$, the value of k'_3/k_3 equals $2/700 = 1/350$ so only once in 350 times does the formation of $\mathrm{Ce\text{-}OH\text{-}H_2}^{+4}$ fail to produce the measured reaction. The value of 0.13 for d gives for $c = ad/b$ a value of $0.13\ (350) = 46$ which is the same within the limits of error as the value of 50 obtained from the slope of the upper line in Fig. 4.

The oxidizing power of $\mathrm{H_2}^+(\mathrm{aq})$ whose existence in the ion $(\mathrm{H_2O})_5\ \mathrm{Ce}^{+4}\text{-}\mathrm{OH}^{-1}\text{-}\mathrm{H_2}^{+1}$ has been postulated can be estimated in the following way.[13] The reaction whose standard potential, E^0, we desire at 25° is (1) $\mathrm{H_2(g)} = \mathrm{H_2}^+(\mathrm{aq}) + \mathrm{e}^-$. If one adds reaction (2) $\mathrm{e}^- + \mathrm{H}^+(\mathrm{aq}) = 1/2\ \mathrm{H_2(g)}$ whose value of E^0 is zero by definition, one obtains reaction (3) $1/2\ \mathrm{H_2(g)} + \mathrm{H}^+(\mathrm{aq}) = \mathrm{H_2}^+(\mathrm{aq})$ whose value of E^0, therefore, equals $E^0{}_1$. In order to estimate a value of E^0 for reaction 3, one may obtain 3 by adding together reactions (4) $1/2\ \mathrm{H_2(g)} + \mathrm{H}^+(\mathrm{g}) = \mathrm{H_2}^+(\mathrm{g})$ and (5) $\mathrm{H_2}^+(\mathrm{g}) + \mathrm{H}^+(\mathrm{aq}) = \mathrm{H_2}^+(\mathrm{aq}) + \mathrm{H}^+(\mathrm{g})$.

In the case of reaction (4), ΔH^0 equals ΔH^0 for $\mathrm{H_2}^+(\mathrm{g}) - [\Delta H^0$ for $1/2\ \mathrm{H_2(g)} + \Delta H^0$ for $\mathrm{H}^+(\mathrm{g})] = 357.15 - [0 + 367.08] = -9.93$ kcal. ΔS^0 for reaction (4) equals $[S^0$ for $\mathrm{H_2}^+(\mathrm{g}) - S^0$ for $\mathrm{H_2(g)}] + [S^0$ for $1/2\ \mathrm{H_2(g)} = 15.6$ e.u.$] - S^0$ for $\mathrm{H}^+(\mathrm{g})$. The difference in brackets equals the difference in rotational entropies of these species plus the term R ln 2 arising from the odd electron on $\mathrm{H_2}^+(\mathrm{g})$. The difference in rotational entropies of $\mathrm{H_2}^+(\mathrm{g})$ and $\mathrm{H_2(g)}$ equals $2R$ ln (1.06/0.74) where the ratio equals the ratio of the radii of $\mathrm{H_2}^+(\mathrm{g})$ and $\mathrm{H_2(g)}$.[14] It follows that S^0 for $\mathrm{H_2}^+(\mathrm{g}) = 31.21 + 2R\ \ln\ (1.06/0.74) + R\ \ln 2 = 34.41$ e.u. The entropy of $\mathrm{H}^+(\mathrm{g})$ is purely translational and may be calculated from the Sackur–Tetrode equation which in this case is $26.00 + (3/2)R\ \ln\ 1.008 = 26.02$ e.u. Thus for reaction (4) at 25° $\Delta S^0 = -7.21$ e.u. and $\Delta F^0 = -9930 - 298(-7.21) = -7.78$ kcal.

In the case of reaction (5), ΔH^0 cannot be calculated because ΔH^0 is not known for $\mathrm{H_2}^+(\mathrm{aq})$. Nevertheless one can estimate an upper and a lower limit for ΔH^0 for this reaction in the following way. At one extreme consider $\mathrm{H_2}^+$ to be an ion like Li^+ which has the same charge and is about the same size. In this case ΔH^0 for reaction 5 would be the same as ΔH^0 for the reaction $\mathrm{Li}^+(\mathrm{g}) + \mathrm{H}^+(\mathrm{aq}) = \mathrm{Li}^+(\mathrm{aq}) + \mathrm{H}^+(\mathrm{g})$ for which $\Delta H^0 = [367.08 + (-66.55)] - [160.86 + 0.0] = +139.7$ kcal. The other extreme is to consider that $\mathrm{H_2}^+(\mathrm{aq})$ has the same energy content as the sum of H(aq) and $\mathrm{H}^+(\mathrm{aq})$ and that ΔH^0 is negligible for the reaction $\mathrm{H(g)} = \mathrm{H(aq)}$. In this case ΔH^0 for reaction (5) would equal ΔH^0 for the reaction $\mathrm{H_2}^+(\mathrm{g}) + \mathrm{H}^+(\mathrm{aq}) = \mathrm{H(aq)}\ \mathrm{H}^+(\mathrm{aq}) + \mathrm{H}^+(\mathrm{g})$ for which $\Delta H^0 = [367.08 + 0 + 52.09] - [357.15 + 0] = +62$ kcal. ΔS^0 for reaction (5) is very nearly zero since the reaction involves the replacement of one gas by a similar gas in the solution. Thus ΔF^0 and ΔH^0 for reaction (5) are very nearly equal so ΔF^0 has a value between +140 and +62 kcal.

The value of ΔF^0 for reaction 3, therefore, has a value between $-7.8 + 140 = 132$ kcal. and $-7.8 + 62 = 54$ kcal. so E^0 for reaction 1 lies between -5.7 and -2.3 volts; hence $\mathrm{H_2}^+(\mathrm{aq})$ is capable of oxidizing cerous to ceric perchlorate since the standard potential for $\mathrm{Ce(III)} = \mathrm{Ce(IV)} + \mathrm{e}^-$ is about -1.7 volts.[6]

The set of reactions given above for the photochemical reduction of water by light absorbed by cerous ions is not necessarily a unique solution to the problem nor does it eliminate the possibility that ceric and other ions whose concentrations were negligible in our solutions may be outstandingly effective as deactivators of the transient species, or that hydrated hydrogen molecule ions may be produced by reaction 2 and subsequently reduced to hydrogen gas largely by oxidizing cerous to ceric ions and to a much lesser extent by oxidizing water to oxygen. The latter possibility exists because of the small amount of oxygen that we have always observed in the hydrogen produced by the reaction although this oxygen may very well have been produced by the oxidation of water by light absorbed by ceric ions.

We have also examined the possibility that the reaction is initiated by light absorbed by a photosensitive cluster consisting of a hydrated ion pair of cerous and hydrogen ions. This hypothesis leads to the conclusion that the ion pair has an association constant of 14 which is incredibly large for a reaction of this kind. The set of reactions given above avoids the formation of this ion pair but replaces it essentially by a similar pair involving a photon activated cerous ion instead of a normal cerous ion; this has the advantage of requiring only the temporary removal of a very small amount of H^+ from $\mathrm{H_3O}^+$ and attributes no unusual properties to acidic solutions of cerous perchlorate in thermal equilibrium with their surroundings.

CAMBRIDGE, MASSACHUSETTS

---

(13) The values of the thermodynamic constants employed here were obtained from W. M. Latimer, "Oxidation Potentials," Ed. 2, Prentice-Hall, New York, N. Y.

(14) The values of the radii were obtained from G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc. New York, N. Y., 1950, p. 532.