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

Quantum Yields of the Photochemical Reduction of Ceric Ions by Water and Evidence for the Dimerization of Ceric Ions

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Water solutions containing ceric perchlorate and perchloric acid evolve oxygen when they absorb ultraviolet light and the ceric is reduced to cerous perchlorate.[2]

Baur[2a] and Weiss and Porret[2b] studied the photochemical reaction in the full light of a quartz mercury arc lamp. Weiss and Porret obtained maximum gross quantum yields of the order of one-tenth in solutions one-tenth molar in ceric perchlorate and one molar in perchloric acid. Their quantum yields decreased as the cerous perchlorate accumulated.

We have measured the quantum yields of the reaction when the solutions are irradiated with monochromatic light of λ 254 mμ. The light intensity, I, and the concentrations of cerous, c_3, and ceric, c_4, perchlorates were varied many fold. The perchloric acid concentration, c_2, was held at 1.03 ± 0.03 M and the ionic strength, μ, at 1.1 ± 0.1, all at 23 ± 3°.

Solutions of ceric perchlorate in perchloric acid are thermally unstable at 25°. The equilibrium ratio c_4/c_3 is about 10^{-8} in molar perchloric acid in equilibrium with the atmosphere ($p_{O_2} = 0.2$ atm.), but the rate of the thermal reduction of the ceric perchlorate by water is extremely slow. In one of our stock solutions which was 5.3 M in perchloric acid and was kept in the dark at 25 ± 3°, c_4 decreased from 1.36 to 1.20 M in eleven months while c_3 increased from 0.32 M.

Materials.—The chemical reagents were of analytical reagent grade or were prepared from material of this quality. The water was chloride-free distilled water.

Stock solutions of ceric and cerous perchlorates were prepared from a sample of snow white granular ceric oxide, 98.5% pure CeO_2, which was supplied by the Rohm and Haas Chemical Co., Philadelphia, Pa.

The ceric oxide could not be converted directly into ceric perchlorate even when dispersed as a fine hydrous oxide in 72% perchloric acid at room temperature or at 100° for periods of several months.

The ceric perchlorate was finally prepared by reducing the ceric oxide to cerous ions by bromide in perchloric acid. The bromine and excess bromide were removed by boiling. The cerous ions were then oxidized electrolytically to the ceric state. The experimental details follow.

Forty grams of the granular ceric oxide and 80 g. of sodium bromide were added to 275 ml. of 72% perchloric acid. The mixture was simmered for two hours under an appropriate hood. The hot solution was filtered by suction through a sintered glass filter. The filtrate was boiled down to half its initial volume; on cooling a colorless solid separated which was removed by decantation and filtering as above. The colorless filtrate, stock solution C, contained 1.68 moles of cerous perchlorate and 5.3 moles of perchloric acid per liter of solution. It contained no material oxidizable by ceric sulfate.

The stock solution B of ceric perchlorate was made by electrolyzing 63 ml. of solution C in a Pyrex beaker. The cylindrical electrodes were of platinum gauze of the type used for copper determinations. They were placed coaxially in the beaker and the smaller electrode was rotated rapidly to stir the solution. The beaker was surrounded by running tap water. The current density was kept for eleven hours at roughly 0.1 amp. per sq. in. of the anode surface. The solution then contained 1.36 moles of ceric perchlorate, 0.32 mole of cerous perchlorate and 5.3 moles of perchloric acid per liter of solution. The concentration of sodium perchlorate in solutions B and C was less than 10/3 the total cerium concentration. About 9.26 moles of sodium perchlorate dissolve in a liter of water solution at 25° and the density of the solution is 1.678 g. per ml.

Analytical Procedures.—The methods of analysis were entirely volumetric. The primary standard of oxidimetry was U. S. Bureau of Standards Sample 40b of sodium oxalate. The primary standard of acidimetry was potassium acid phthalate.

The cerous, ceric and acid concentrations were determined by essentially the same procedures used by M. S. Sherrill, C. B. King and R. C. Spooner.[3] Several modifications require mention. In determining c_4, 2 ml. of concd. sulfuric acid were added to each 5 ml. sample analyzed and the resulting solution after mixing was either titrated immediately or heated in boiling water for five minutes. Five or ten drops (0.25 or 0.50 ml.) of 0.0043 M orthophenanthroline indicator were used to identify the end-point in each analysis. The titrations were carried out with ferrous sulfate or ferrocyanide solutions. End-points were reproduced at best to $\pm 10^{-7}$ mole of ceric ion. This was accomplished by using similar test-tubes for all the titrations and viewing the solutions end on against a white illuminated background.

The actinometer solutions of uranyl oxalate were titrated at 80° with permanganate solution after adding 2 ml. of 4 N sulfuric acid per 10 ml. of the oxalate sample. End-points were determined to $\pm 10^{-8}$ mole of oxalate by means of the differential electrometric method previously developed.[4] Care was taken to minimize even local excesses of the permanganate until the end-point was reached.

Absorption spectra of the solutions were mapped out by means of a Hilger sector photometer backed by a quartz spectrograph. The cerous solutions were colorless, the ceric solutions ranged from colorless in the case of the most dilute solutions to amber in the case of the most concentrated solutions.

Extinction coefficients, ϵ, were measured in the region of λ, 254 mμ by means of a Beckman ultraviolet spectrophotometer. Values of ϵ were calculated by means of the equation $\epsilon = (1/cd) \log_{10} (I_0/I)$ when c is the concentration of the solute in moles per liter of solution, I_0 and I are the intensities of the light beams after traversing equal depths, d in cm., of the solvent and solution, respectively. Water, perchloric acid and sodium perchlorate absorbed a negligible amount of light of λ, 254 mμ in the cerous and ceric solutions over the range of concentrations and depths

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[1] The part of this article concerned with the experimental study of the effect of cerous perchlorate upon the reaction is taken from the thesis submitted by Maynard E. Smith in September, 1946, to the Department of Chemistry of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

[2] (a) E. Baur, *Z. physik. Chem.*, **63**, 683 (1908), was the first to identify oxygen as the gaseous product of the reaction. This was ater confirmed by (b) J. Weiss and D. Porret, *Nature*, **139**, 1019 (1937).

[3] M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

[4] L. J. Heidt, *ibid.*, **61**, 3455 (1939).

TABLE I

EXTINCTION COEFFICIENTS, ϵ, OF CEROUS AND CERIC PERCHLORATES IN 1.03 ± 0.03 *M* PERCHLORIC ACID AT 23 ± 3°

c_4	c_3	c_4/c_3	ϵ at λ, 253	254	255 mμ
0	0.00007 to 0.03	0	ϵ_3, 760 ± 70	750 ± 70	740 ± 70
0.0006 to 0.0094		2.5	ϵ_4, 1750 ± 90	1710 ± 95	1670 ± 90
0.0007 to 0.0043		.78	ϵ_4, 1740 ± 110	1680 ± 120	1610 ± 80
0.0024		.42	ϵ_4, 1790 ± 20	1750 ± 20	1660 ± 20
0.0009 to 0.0023		.22	ϵ_4, 1765 ± 85	1700 ± 20	1540 ± 60

The average value of ϵ_4 is 1730 and of ϵ_3 is 750.

employed. The solutions obeyed Beer's law, *i. e.*, $\epsilon c = \epsilon_3 c_3 + \epsilon_4 c_3$ within the limits given in Table I.

Quantum yields were determined for monochromatic light of λ 254 mμ. The apparatus has been described.[5] It has been shown[5] that the light of λ 185 mμ produced by the lamp is completely (more than 99.99%) absorbed between the lamp and the reaction vessel by the two-cm. layer of running tap water and the cylindrical clear fused quartz filter containing a one-cm. layer of chlorine gas at one atm. A one-cm. layer of glacial acetic acid produced the same results.

Two sets of transparent fused quartz cylindrical reaction vessels were employed. In one set the cells had diameters of 1.3 cm and each held 11 ml. when filled to the neck. In the other set the diameters ranged from 2.4 to 2.8 cm. and each held 42 ml. when filled to the neck. The transmission of light of λ 254 mμ by the cell walls of all the reaction vessels was the same within 1%. The stirrers were made of transparent fused quartz ribbon and were rotated on the axes of the cells.

Concentrations of cerous and ceric perchlorates were limited to those that absorbed over 90% of the light of λ 254 mμ incident on the solutions before the light reached the stirrer. Less than 1% of this light emerged from any reaction cell.

Light fluxes incident upon the solutions were measured with the uranyl oxalate actinometer first standardized by W. G. Leighton and G. S. Forbes.[6] The actinometer solution for the 11 ml. cells contained 0.0017 mole of uranyl oxalate and 0.0040 mole of oxalic acid per liter of solution, and for the 42 ml. cells it was half this strength.

Light fluxes were determined at the beginning, middle and end of each day of work or more often if the light flux was believed to be varying more than 5%. The duration of each photolysis was measured to the nearest second. Up to 20% of the oxalate and 16% of the ceric concentrations were destroyed by photolysis.

The photochemical data are given in terms of the quantum yield, ϕ, of the reaction, *i. e.*, the moles of ceric perchlorate reduced to cerous perchlorate per mole of light quanta absorbed only by the ceric perchlorate. The pertinent data are given in Table II. $\phi_{\text{gross}} = V\Delta c_4/E$, $\phi = \phi_{\text{gross}}$ $(1730\ c_4 + 750\ c_3)/1730\ c_4$, $\phi^* = \phi_{\text{gross}}\ (1730\ c_4 + 750\ c_3)/750\ c_3$. V is the volume in liters of the solution irradiated, Δc_4 is the change in the molar concentration of the ceric perchlorate produced by the irradiation, and E is the fraction of an einstein (6×10^{23} quanta) of light of λ, 254 mμ absorbed by the solution irradiated. The starred values refer to cerous instead of ceric perchlorate.

The values given in Table II for c_3, c_4 and the perchloric acid concentration are the average values during photolysis. The symbol c_4^0 refers to the value of concentration of ceric perchlorate in the unphotolyzed sample. The number in parentheses following the gross quantum yield indicates the number of expts upon which the values in that row are based. The column headed 10^6 E/min. gives the average light flux of λ 254 mμ incident upon the solutions irradiated; in all cases except expt. 1, this value also equals the light flux absorbed by the solution.

In expt. 1, the irradiation of the perchloric acid produced no detectable substances which either oxidized ferrocyanide or reduced permanganate in dilute sulfuric acid.

In two sets of experiments with a solution like that used in expt. 5, ϕ gross remained constant within 4% when the light intensity was changed 1/3.7 by dimming the lamp by means of a variac in the lamp circuit.

Two different methods were employed to change the concentration of cerous perchlorate. In expts. 11 and 14, appropriate amounts of the ceric perchlorate solution in which c_4/c_3 was about three were reduced with hydrogen peroxide free of preservative until c_4 equalled about 0.012. In all the other expts. appropriate amounts of the ceric and cerous stock solutions B and C were mixed. Both methods produced the same results.

The effect of cerous perchlorate upon the reaction is shown in Fig. 1. A decrease in the quantum yield, ϕ, is seen to be produced by an increase in the concentration of cerous perchlorate, *i. e.*, a decrease in the ratio of ceric to cerous perchlorate when other variables are held constant. Cerous perchlorate absorbs ultraviolet light of λ 254 mμ but since ϕ is based upon the light of this wave length absorbed only by the ceric perchlorate, the value of ϕ would have remained unchanged if the cerous perchlorate acted only as an inner filter. The line passing through the data is based on the hypothesis that the cerous perchlorate deactivates the photon activated ceric ions.

The line in Fig. 1 was determined by a plot of $1/\phi$ *vs.* c_3. The data on such a plot fall on a straight line within the limits of error. The line

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[5] L. J. Heidt, *Science*, **90**, 472 (1939).

[6] (a) W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930); see also (b) L. J. Heidt, *J. Phys. Chem.*, **40**, 624 (1942).

TABLE II

GROSS AND NET QUANTUM YIELDS AT 23 ± 3° FOR THE PHOTOLYSIS OF CERIC AND CEROUS PERCHLORATES IN 1.03 ± 0.03 *M* PERCHLORIC ACID AT IONIC STRENGTHS OF 1.1 ± 0.2, BY LIGHT OF λ 254 mμ

Expt.	c_3	c_4	c_4/c_3	Cell vol., l.	Min.	$\Delta c_4/c_4^0$	10^6 *E*/min.	ϕ_{gross}	ϕ
1	0.00000	0.00000	0.00000	0.011	1020	0.00000	5.9	0.00000(2)	0.0000
2	.00045	.00123	2.72	.042	9.0	.162	25.6	.040 (2)	.0464
3	.00102	.00234	2.30	.042	8.0	.125	26.4	.062 (2)	.0736
4	.00207	.00465	2.25	.042	6.0	.0794	28.4	.095 (2)	.113
5	.00358	.00987	2.76	.042	3.3	.0655	71.3	.118 (3)	.136
6	.00357	.01088	3.04	.011	15.0	.0795	6.01	.110 (2)	.125
7	.00285	.0106	3.72	.011	15.5	.129	8.07	.128 (4)	.143
8	.00696	.01638	2.35	.011	25.0	.0595	3.62	.122 (2)	.145
9	.00637	.01105	1.73	.011	15.0	.0627	5.7	.092 (2)	.115
10	.00655	.01088	1.66	.011	20.0	.0887	6.6	.084 (2)	.106
11	.0135	.0113	0.835	.042	9.0	.025	29.3	.046 (2)	.070
12	.01502	.01113	.74	.011	15.0	.0505	10.1	.042 (2)	.066
13	.0340	.0112	.33	.011	30.0	.0212	7.1	.0124 (2)	.0287
14	.0540	.0120	.222	.042	15.0	.01335	36.1	.0125 (2)	.0369
15	.00238	.00012	.0050	.011	815	.0096*	11.2	.00029(2)	.00029*
16	.0098	.000196	.0020	.011	1033	.0093*	10.9	.00038(2)	.00038*
17	.0394	.000401	.0012	.011	1307	.00202*	10.4	.00065(1)	.00065*
18	.0792	.000244	.000307	.011	1295	.000613*	12.1	.00034(2)	.00034*

intercepts the $1/\phi$ axis at 5 ± 0.2 and has a slope, $(1/\phi)/c_3$, of 670 ± 50; hence $1/\phi = 5 + 670\ c_3$ and $\phi = 1/(5 + 670\ c_3)$ for these data.

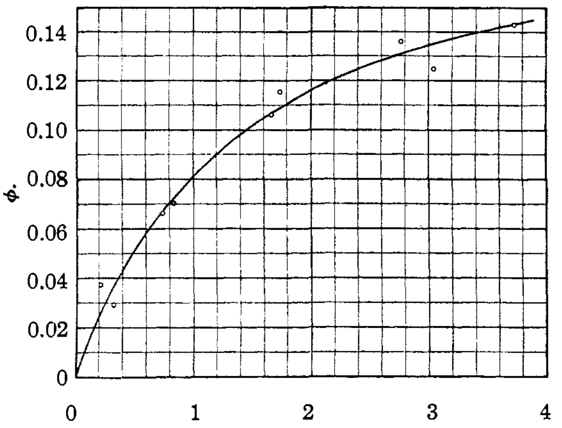

Fig. 1.—$c_2 = 1.03 \pm 0.003$, $c_4 = 0.0110 \pm 0.00045$, $\mu = 1.2 \pm 0.1$.

The possibility that the changes in ϕ are produced by changes in the light flux absorbed by the ceric perchlorate is eliminated by the finding noted above that ϕ did not change when the light intensity was changed several-fold while other variables were held constant.

There remains, however, the possibility that the quantum yields, ϕ, are decreased by cerous ions because the light absorbed by them causes them to be oxidized to ceric ions. The data in expts. 15, 16, 17 and 18 show that this reaction does occur and that the quantum yield, ϕ^*, of the reaction is about 0.001 in 0.06 molar cerous perchlorate. This value of ϕ^* is, however, less than 1% of the total decrease of 0.12 produced in ϕ by this concentration of cerous perchlorate in 0.011 molar ceric perchlorate, so the main effect of the cerous ion is to deactivate ceric ions. The decrease of 0.12 in ϕ is obtained from Fig. 1 where ϕ drops from 0.15 to 0.03 when c_4/c_3 decreases from 4 to 0.2 while the concentration of ceric perchlorate remains at 0.011 molar.

The photochemical oxidation of cerous to ceric perchlorate in expts. 15, 16, 17 and 18 was made evident by the orange color of ceric sulfate produced in the photolyzed but not in the unphotolyzed solutions when they were treated with concentrated sulfuric acid in the course of the analysis of them for ceric ions. The intensity of the orange color which developed in the solutions was directly proportional to the amount of ferrous ion required to bleach them. We did not test for hydrogen produced by the photoxidation of the cerous ions, but it is worth noting that when $\epsilon_3 c_3 \phi^* = \epsilon_4 c_4 \phi$, the amounts of cerous and ceric perchlorates in the solution being irradiated would remain unchanged while water was being broken down into oxygen and hydrogen.

Figure 2 shows that an increase in the net quantum yield ϕ accompanies an increase in c_4. The increase occurs in spite of an accompanying increase in c_3 since in the case of these data c_4/c_3 is nearly constant at 2.8. It is not caused by the increase in the concentration of photon activated ceric perchlorate because ϕ was found not to depend upon the light intensity. The line passing through the data is based on the hypothesis that only light absorbed by ceric dimers produces the measured reaction. The dependence of ϕ upon c_4 and c_3 is then given by the equation $\phi = y/(a + bc_3)$ where y is the fraction of the ceric ions dimerized and a and b are constants. $y/(1 - y)^2 = 2K_pc_4$ where K_p is a constant under the prevailing conditions. The last equation for ϕ is repre-

TABLE III

MOLAL POTENTIALS E_1^0 AT 25° FOR THE REACTION $CeOH^{+3} + {}^1/_2H_2 = Ce^{+3} + H_2O$

Calculated from the data of Sherrill, King and Spooner at a perchloric acid concentration of 0.8 *M*. The values of $^*E_1^0$ have allowed for the dimerization of ceric ions. The symbols are explained in the text.

c_2	10^3c_4	c_4/c_3	$10^3\,{}^0c'_m$	$10^3\,c'_m$	E	E_f^0	E_1^0	$^*E_1^0$
0.8024	8.436	5.4531	4.827	2.884	1.73219	1.68301	1.7023	1.7155
.8036	6.572	1.9312	3.763	2.549	1.70970	1.68721	1.7072	1.7167
.8038	5.698	1.3351	3.263	2.319	1.70110	1.68810	1.7080	1.7168
.8048	3.968	0.6626	2.273	1.742	1.68456	1.68958	1.7095	1.7163
.8075					Extr.	1.6930	1.7128	

sented by the line in Fig. 2 when K_p equals 50, and a/y and b/y equal 5 and 670, respectively, from the data in Fig. 1.

The value of K_p was estimated by the method of successive approximations. This involved evaluating c_4 for various values of y and K_p. Next, a and b were evaluated for the values of y at $c_4 = 0.011$. Then ϕ was calculated for the values of c_4 covered by the data. Values of K_p equal to 50 ± 10 fit the data within the limits of error, but when K_p is set equal to 100 or 25 the calculated values of ϕ fall well outside the limits of error especially at the lower values of c_4.

A value of 50 for K_p gives a value of 0.398 for y at c_4 equal to 0.011 and the corresponding values of a and b are 2 and 270, respectively.

The tendency of the observed values of ϕ to fall above the line in Fig. 2 at the highest concentrations of ceric perchlorate suggests that photosensitive trimers and higher polymers of ceric ions are also formed in these solutions.

The nature of ceric monomers in perchloric acid has been postulated by Professor M. S. Sherrill[3] based on e. m. f. data on these solutions. The formulas postulated are $CeOH^{+3}$ and $Ce(OH)_2^{+2}$. The equilibrium constant for the reaction $CeOH^{+3} + H_2O = Ce(OH)_2^{+3} + H^+$ was found to be 0.6. A slight extension of this idea suggests that the formulas of the dimers are $Ce{-}O{-}Ce^{+6}$, $HOCe{-}O{-}CeOH^{+4}$ and $Ce{-}O{-}CeOH^{+5}$. The formation of the dimers would be expected to take place by splitting out water from the hydroxyls attached to separate ceric monomers. The same kind of reaction would also produce trimers and higher polymers involving the $Ce(OH)_2^{+2}$ ion.

The formation of ceric dimers in ceric perchlorate solutions is also supported by the e. m. f. measurements of M. S. Sherrill, C. B. King and R. C. Spooner.[3] The solutions in their Run III are nearest in composition to our solutions; the main difference is that their perchloric acid concentration, c_2, was 0.8 compared to 1.03 *M* in our work.

The e. m. f. measurements were made on the cell H_2, $HClO_4$ at c_1/c_2, c_3, c_4 Pt. This cell can be thought of as two cells connected in series, namely, cell I, H_2, c_1/c_2, H_2, and cell II, H_2, c_2/c_2, c_3, c_4 Pt. The first of these cells has a liquid junction potential $E_L = (2T_{H^+} - 1)\ 0.05915 \log (c_1\gamma_1/c_2\gamma_2)$ or very nearly $E_L = (0.6744)\ 0.05915 \log (c_1/c_2) = 0.03989 \log (c_1/c_2)$ as calculated by S. K. S. The observed e. m. f. values, E, were corrected to hydrogen at 1 atm. and 25°. Table III gives the data for their Run III.

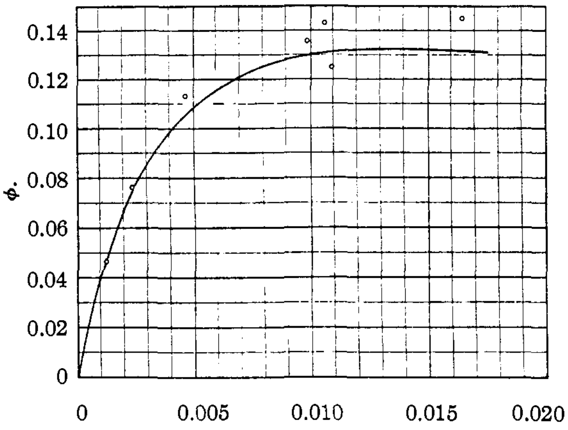

Fig. 2.—$c_2 = 1.03 \pm 0.3$, $c_4/c_3 = 2.80 \pm 0.26$, $\mu = 1.1 \pm 0.1$.

The formal potential E_f^0 $(= E - 0.05915 \log (c_4/c_1c_3) - E_L)$ includes the liquid junction potential E_L' produced by c_3 and c_4 in c_2 of Cell II and in addition a term involving the activity coefficients of the various species in the solutions.

Constant values of 1.7134 ± 0.0004 volts were obtained by S. K. S. for the molal potential E_1^0 of the reaction $CeOH^{+3} + {}^1/_2H_2 = Ce^{+3} + H_2O$ when c_2 is between 0.54 and 1.6 *M* and $c_4 = {}^0c'_m + {}^0c''_m$, ${}^0c''_m/{}^0c'_m = 0.6/c_2$ and $E_1^0 = E_f^0(\text{extr.}) + 0.05915 \log (c_4/c_2{}^0c'_m)$. The symbols ${}^0c'_m$ and ${}^0c''_m$ represent the concentrations of $CeOH^{+3}$ and $Ce(OH)_2^{+2}$, respectively, when there is no dimerization. The symbol E_f^0(extr.) represents the value obtained for E_f^0 when extrapolated to $c_4/(c_3 + c_4)$ equal to zero. The value of E_1^0 calculated from E_f^0 at any actual value of c_4 is always less than the value calculated from E_f^0 (extr.), and it increases as c_4 decreases as shown in Table III. This trend is eliminated when allowance is made for the dimerization of ceric ions. The values of E_1^0 corrected for this effect are the $^*E_1^0$ values in Table III.

$$^*E_1^0 = E_f^0 + 0.05915 \log (c_4/c_2c'_m)$$

TABLE IV

THE VALUES OF $*E_1^0$ FOR THE SEPARATE E. M. F. RUNS MADE BY SHERRILL, KING AND SPOONER. THE AVERAGE VALUE OF $*E_1^0$ IS 1.7174; IT IS 1.7169 WHEN RUN V IS OMITTED

Run	Expts.	c_2	c_4	$*E_1^0$
V	6	0.1973 ± 0.0018	0.0010 to 0.0093	1.72074 ± 0.00085
IV	5	.4787 ± .0016	.0010 to .0086	1.71793 ± .00072
VII	2	.5325 ± .0015	.0032 to .0072	1.71853 ± .00057
VIII	4	.5347 ± .0011	.0009 to .0055	1.71584 ± .00041
III	4	.8036 ± .0007	.0040 to .0084	1.71633 ± .00043
IX	3	1.2977 ± .0007	.0010 to .0045	1.71530 ± .00038
II	2	1.6304 ± .0007	.0032 to .0048	1.71664 ± .00024
I	2	2.3841 ± .0014	.0048 to .0066	1.71751 ± .00026

where

$$c_4 = c'_m + c''_m + 2c_p$$
$$c'_m + c''_m = \sqrt{c_p/50}, \text{ and}$$
$$c'_m/c''_m = 0.6/c_2$$

The values of $*E_1^0$ for the separate runs in the order of increasing acid strength, c_2, are given in Table IV.

The average value of $*E_1^0$ for Run V is significantly higher than the other values and the ionic strength, μ, is the lowest (μ equals 0.26 compared to 0.5 to 2.4 in the other runs). An increase in the value of $*E_1^0$ would be produced if the activity of $CeOH^{+3}$ decreased with μ. This can be seen by comparing the values of E_1^0 and $*E_1^0$ in Table III. The higher values of $*E_1^0$ in Table III are associated with the lower values of the activity of the $CeOH^{+3}$ which resulted from the correction for the dimerization. A decrease in μ favors the hydrolysis of $CeOH^{+3}$ but it also favors a decrease in the dimerization. The two effects thus tend to cancel each other and this is supported by the lack of any trend in the values of $*E_1^0$ in Table IV with changes in μ between 0.5 and 2.4.

Empirically, the values of $*E_1^0$ depend linearly upon the logarithm of $(c_2 + 3c_3 + 4c_4)/c_2$, as is shown in Fig. 3. The equation for the line in the Fig. is $*E_1^0 = (1.71545 \pm 0.00026) + (0.06185 \pm 0.00594) \log [(c_2 + 3c_3 + 4c_4)/c_2]$. The probable deviation of any value of $*E_1^0$ from the line is 0.00082.

The molal oxidation potential E_1^0 of the electrode reaction (1) $CeOH^{+3} + H^+ + E^- = Ce^{+3} + H_2O$ obtained by the above method is 1.7155 instead of 1.7134 volts obtained from $E^0{}_f$(extr.).

The molal oxidation potentials of the other

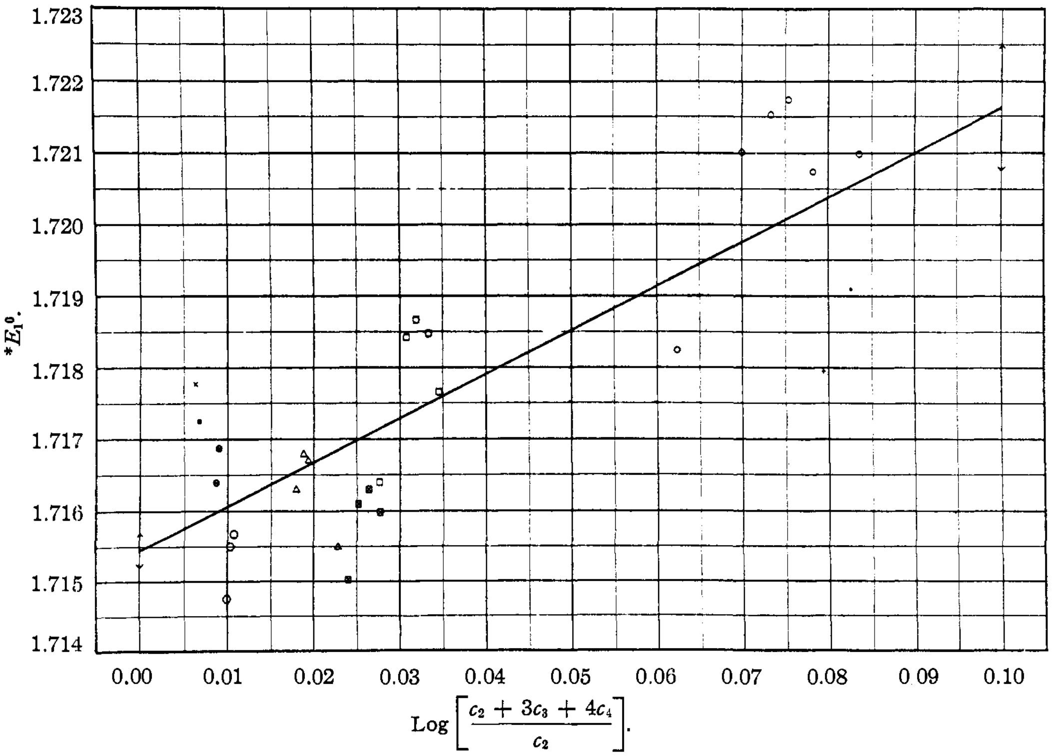

Fig. 3.—○, c_2 = 0.197; □, c_2 = 0.479; +, c_2 = 0.532; ⊠, c_2 = 0.535; △, c_2 = 0.803; ⬡, c_2 = 1.297; ⊗, c_2 = 1.630; ×, c_2 = 2.384.

TABLE V

CONCENTRATIONS OF THE VARIOUS CERIC SPECIES PRESENT AT 25° OVER THE RANGE OF CONCENTRATIONS COVERED BY THE QUANTUM YIELD MEASUREMENTS

$c_2 = 1.03$; $c_p/c_m^2 = y/(1-y)^2 2c_4 = 50$; $c'_m = (\text{CeOH}^{+3}) = c_m/(1 + 0.6/c_2) = c_m/1.583$; $c''_m = (\text{Ce(OH)}_2{}^{+2}) = c_m - c'_m$; $c_{1p} = (\text{Ce—O—Ce}^{+6}) = 50(c'_m)^2$; $c_{2p} = (\text{HOCe—O—Ce—OH}^{+4}) = 50(c''_m)^2$; $c_{1,2p} = (\text{Ce—O—Ce—OH}^{+5}) = 100c'_m\, c''_m$

c_4	y	$10^3\, c_p$	$10^3\, c_m$	$10^3\, c'_m$	$10^3\, c''_m$	$10^5\, c_{1p}$	$10^3\, c_{2p}$	$10^5\, c_{1,2p}$
0.000102	0.010	0.00051	0.101	0.0638	0.0372	0.020	0.00692	0.024
.00101	.085	0.043	0.924	0.583	0.341	1.7	0.58	1.99
.0102	.385	1.96	6.23	3.94	2.29	78	26	91
.0149	.450	3.35	8.20	5.18	3.02	134	46	156

electrode reactions on the above basis are:

(2) $\text{Ce(OH)}_2{}^{+2} + 2\text{H}^+ + E^- = \text{Ce}^{+++} + 2\text{H}_2\text{O}$; $E_2{}^0 = 1.7286$ volts

(1p) $0.5\ \text{Ce—O—Ce}^{+6} + \text{H}^+ + E^- = \text{Ce}^{+++} + 0.5\ \text{H}_2\text{O}$; $E_{1p}{}^0 = 1.6652$ volts

(2p) $0.5\ \text{HO—Ce—O—Ce—OH}^{+4} + 2\text{H}^+ + E^- = \text{Ce}^{+++} + 1.5\ \text{H}_2\text{O}$; $E_{2p}{}^0 = 1.6783$ volts

(1,2p) $0.5\ \text{Ce—O—CeOH}^{+1} + 1.5\text{H}^+ + E^- = \text{Ce}^{+++} + \text{H}_2\text{O}$; $E^0{}_{(1,2p)} = 1.6628$ volts

$$E_2{}^0 = E_1{}^0 - 0.05915 \log 0.6$$
$$E_{1p}{}^0 = E_1{}^0 - 0.05915 \log \sqrt{K_{1p}}$$
$$E_{2p}{}^0 = E_2{}^0 - 0.05915 \log \sqrt{K_{2p}}$$
$$E_{1,}{}^0{}_{2p} = (E_1{}^0 + E_2{}^0)/2 - 0.05915 \log \sqrt{K_{1,2p}}$$
$$K_{1p} = K_{2p} = K_{1,2p}/2 = 50$$

within the limits of error of either the quantum yield measurements or the e. m. f. data.

The compositions of the ceric perchlorate solutions over the range covered by the quantum yield measurements are given in Table V.

The following reactions in addition to the equilibria given above account for the quantum yields.

K_p	$2c_m = c_p$
k_I	$c_p + h\nu = c_p{}^*$
k_1	$c_p{}^* + \text{H}_2\text{O} = 2c_3 + 2\text{H}^+ + {}^1/{}_2\text{O}_2$
k_2	$c_p{}^* + c_3 = c_p + c_3$
k_3	$c_p{}^* + S = c_p + c_3$

c_m is the concentration of all the ceric monomers

c_p is the concentration of all the ceric dimers

S is any substance except c_3; the solutions do not fluoresce

k_1, k_2, and k_3 are the rate constants for the corresponding reactions

The reactions give a maximum quantum yield of two and the following equation for ϕ

$$\phi = 2yk_1/(k_1 + k_3S + k_2c_3)$$

or

$$\phi = y/(a + bc_3) \text{ at constant ionic strength}$$
$$a = (k_1 + k_3S)/2k_1 = 2.0$$
$$b = k_2/2k_1 = 270$$

Thus the deactivation of the photon-activated ceric dimer by cerous ions is 2 × 55.5 × 2.70 or 30,000 times more efficient at 25° than the reduction of the dimer by water. The remainder of the environment, however, reacts with the photon-activated dimer little more efficiently ($k_3S/k'_1 \cdot (\text{H}_2\text{O}) = 3$) than the measured photochemical reaction.

Our initial interest in the photochemistry of the ceric perchlorate system was to learn something about the way in which water is photochemically oxidized to oxygen since this oxidation is a fundamental step in the photosynthetic process in living organisms. The work above shows that light absorbed by ceric monomers has a negligible effect upon the reaction. This implies that divalent oxygen is not photochemically oxidized unless the photon activated ceric unit can absorb two electrons from the oxygen. There is no evidence for the intermediate formation of peroxide in the photochemical oxidation of divalent oxygen either in the present research or when the photon activated unit is the persulfate anion,[7] $\text{S}_2\text{O}_8{}^=$. In the latter case all tests for the photochemical formation of hydrogen peroxide along with the oxygen were negative although hydrogen peroxide is made thermally from persulfates.

Summary

1. Photolysis of ceric perchlorate in perchloric acid has been measured quantitatively in ultraviolet monochromatic light of λ 254 mμ.

2. Net quantum yields, ϕ, based on the light absorbed by the ceric perchlorate depend on the concentrations of cerous, c_3, and ceric perchlorates. The dependence is given by the equation $\phi = y/(a + bc_3)$ where y is the fraction of ceric ions dimerized and a and b are constants. ϕ does not depend upon the light intensity, and is negligible for ceric monomers.

3. The dimerization of ceric ions is also supported by e. m. f. measurements on solutions of cerous and ceric perchlorates in perchloric acid, but it is not revealed by measurements of the extinction coefficients of the solutions in the region of λ 254 mμ.

4. The molal oxidation potentials of the various cerium species are calculated.

5. Cerous ions were found to be photochemically oxidized to ceric ions.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 24, 1948

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[7] L. J. Heidt, *J. Chem. Phys.*, **10**, 297 (1942).