[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Spectrophotometric Investigation of the Cerium(IV)–Chromium(VI) Complex Ion Equilibria in Perchloric Acid Solution[1,2,3a]

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RECEIVED NOVEMBER 23, 1953

Spectrophotometric measurements upon 1.00 molar perchloric acid solutions containing cerium(IV) and chromium(VI) at 25° demonstrate the existence of a complex ion involving one cerium(IV) atom and one chromium(VI) atom. Since the measurements were made at this one acidity only, it was not possible to establish the net charge upon the complex. The value of the apparent equilibrium quotient K (defined in Table II) has been obtained from the spectral data. If the 1:1 complex ion has the formula $CeCrO_4^{++}$, the value of the equilibrium quotient $(CeCrO_4^{++})/(Ce^{+4})(CrO_4^{=})$ may be calculated from the value of K. The value, so obtained, is larger than the value of the corresponding equilibrium quotient for the $CeSO_4^{++}$ complex ion by a factor of approximately 10^7.

A preliminary spectrophotometric investigation,[4] in which the method of continuous variation[5] was used, demonstrated the existence of a complex ion involving cerium(IV) and chromium(VI) with an atomic ratio of one-to-one. A number of complications exist which make the quantitative investigation of this system more difficult than the usual investigation of a complex ion equilibrium by spectrophotometric means. These are the existence of monomer–dimer equilibria in perchloric acid solutions for both cerium(IV)[6] and chromium(VI),[7] and the fact that all of the cerium(IV) and chromium(VI) species absorb light to a significant extent compared to the absorption of the complex at the wave lengths at which the measurements are most conveniently carried out. The present measurements have been made upon solutions of a single acidity and medium, one molar perchloric acid; this is the only medium in which the monomer–dimer equilibrium for both cerium(IV)[6a] and chromium(VI)[7b] have been elucidated.

Experimental

In the present study, the optical density of a number of 1.00 M perchloric acid solutions containing cerium(IV) and chromium(VI) have been determined at 25.0 ± 0.2° at the wave lengths 370, 380, 390 and 400 mμ. The compositions of these solutions are summarized in Table I, and the symbols and definitions used in this paper are given in Table II. The evidence for an interaction between cerium(IV) and chromium(VI) is striking: the light absorption at 390 mμ of the solutions used in the evaluation of the equilibrium quotient was generally between two- and threefold higher than would be expected on the basis of no interaction. The several series of data have been used in different ways. The value of K has been derived from measurements upon the solutions of series a-d at 390 **mμ.** The first approximation to the value of $\epsilon_{Ce_1Cr_1}$ at 390 mμ was obtained from the measurement on the solution of series f. The remaining data have been used in the evaluation of the extinction coefficient of the complex at the other wave lengths and in checking the consistency between the observed values of the optical density and the values calculated using the derived values of the parameters K and $\epsilon_{Ce_1Cr_1}$.

TABLE I

SUMMARY OF CONCENTRATION CONDITIONS[a] WHICH EXISTED IN THE SOLUTIONS STUDIED

All solutions: 1.00 M $HClO_4$

	$[Ce^{IV}] \times 10^4$	$[Ce^{III}] \times 10^4$	$[Cr^{VI}] \times 10^4$ (range)	No. of soln.
a	9.50	1.30	4.92–49.2	6
b	9.60	1.20	24.6–44.3	5
c	24.1	2.9	4.92–22.2	8
d	47.5	6.5	4.38–19.7	8
e	96.0	12.0	2.46–9.84	6
f	142.6	19.5	9.84	1

[a] All concentrations are given in gram atoms per liter.

TABLE II

SYMBOLS AND DEFINITIONS[a]

K = $(Ce_1Cr_1)/(Ce_1)(Cr_1)$
K'' = $(Ce_2)/(Ce_1)^2$, the dimerization quotient of cerium(IV)
K' = $(Cr_2)/(Cr_1)^2$, the dimerization quotient of chromium(VI)
(Ce_1) = total concn. of monomeric cerium(IV) species
(Cr_1) = total concn. of monomeric chromium(VI) species
(Ce_2) = total concn. of dimeric cerium(IV) species
(Cr_2) = total concn. of dimeric chromium(VI) species
(Ce_1Cr_1) = total concn. of the 1:1 complex ion
$[Ce]$ = total concn. of cerium(IV)
$[Cr]$ = total concn. of chromium(VI)
D = $\log (I_0/I)$
l = absorption cell length in cm.
ϵ_X = apparent extinction coefficient of the X species

[a] The concentrations of uncomplexed cerium(IV) and chromium(VI) species are expressed in gram atoms per liter. Because of this, K' defined here has a value 2 times the analogous K' of reference 7b, and K'' has 2 times the dimerization quotients presented in 6a,b,c. All extinction coefficients of uncomplexed species are calculated on a gram atom per liter concentration basis. The extinction coefficient of the complex is calculated on the molar concentration basis.

Treatment of Data.—Since the studies being reported here were carried out at a single concentration of hydrogen ion (1.00 M), these data do not provide information regarding the charge on the complex. That is, the complex ion may involve hydrogen ion and/or hydroxide ion in addition to Ce^{+4} and $CrO_4^{=}$; possible 1:1 complex ions are $Ce(OH)(CrO_4)^+$, $CeCrO_4^{++}$ and $CeCrO_4H^{+++}$. At this particular acidity, significant amounts of

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(1) This work has been supported in part by the United States Atomic Energy Commission.

(2) Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(3) (a) From the Ph.D. thesis of James Y.-P. Tong, University of Wisconsin, 1953. (b) Durez Plastics and Chemicals, Inc., Research Laboratory, Le Roy, N. Y.

(4) L. F. Meadows, unpublished work, University of Wisconsin, (1951).

(5a) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(5b) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

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

(6b) T. J. Hardwicke and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

(6c) E. L. King and M. L. Pandow, THIS JOURNAL, **74**, 1966 (1952).

(7a) J. D. Neuss and W. Rieman, *ibid.*, **56**, 2238 (1934).

(7b) J. Y.-P. Tong and E. L. King, *ibid.*, **75**, 6180 (1953).

more than one of the complex ions may be present. The value of the apparent equilibrium quotient K

$$K = \frac{(\mathrm{Ce_1Cr_1})}{(\mathrm{Ce_1})(\mathrm{Cr_1})} \qquad (1)$$

is constant in spite of the existence of the several species of monomeric cerium(IV), monomeric chromium(VI) and possibly the complex, because the relative concentrations of the several monomeric species of each constituent, cerium(IV) or chromium(VI), and of the 1:1 complex have constant values at any one particular acidity. In 1 M perchloric acid, the uncomplexed monomeric species exist in the relative proportions: 0.45 as H_2CrO_4, 0.55 as $HCrO_4^-$ and $10^{-4}\%$ as $CrO_4^{=}$; 0.1 as Ce^{+4}, 0.5_5 as $CeOH^{+++}$, and 0.3_5 as $Ce(OH)_2^{++}$.[8]

It is possible to derive equations for the evaluation of the apparent equilibrium quotient, K, from the observed optical density data. The definitions and material balance considerations lead to

$$(\mathrm{Cr_2}) = K'(\mathrm{Cr_1})^2 \qquad (2)$$

$$(\mathrm{Ce_1Cr_1}) = [\mathrm{Cr}] - (\mathrm{Cr_1}) - K'(\mathrm{Cr_1})^2 \qquad (3)$$

$$\begin{aligned}(\mathrm{Ce_2}) &= [\mathrm{Ce}] - (\mathrm{Ce_1}) - (\mathrm{Ce_1Cr_1}) \\ &= [\mathrm{Ce}] - (\mathrm{Ce_1}) - [\mathrm{Cr}] + (\mathrm{Cr_1}) + K'(\mathrm{Cr_1})^2 \qquad (4)\end{aligned}$$

Equating the observed optical density (per unit of light path length) to the sum of the contributions from the several absorbing species gives

$$D/l = (\mathrm{Ce_2})\epsilon_{\mathrm{Ce_2}} + (\mathrm{Ce_1})\epsilon_{\mathrm{Ce_1}} + (\mathrm{Cr_2})\epsilon_{\mathrm{Cr_2}} + (\mathrm{Cr_1})\epsilon_{\mathrm{Cr_1}} + (\mathrm{Ce_1Cr_1})\epsilon_{\mathrm{Ce_1Cr_1}} \qquad (5)$$

which leads to

$$\begin{aligned}D/l = {}&\epsilon_{\mathrm{Ce_2}}\{[\mathrm{Ce}] - (\mathrm{Ce_1}) - [\mathrm{Cr}] + (\mathrm{Cr_1}) + K'(\mathrm{Cr_1})^2\} + \\ &\epsilon_{\mathrm{Ce_1}}(\mathrm{Ce_1}) + \epsilon_{\mathrm{Cr_2}}K'(\mathrm{Cr_1})^2 + \epsilon_{\mathrm{Cr_1}}(\mathrm{Cr_1}) + \epsilon_{\mathrm{Ce_1Cr_1}}\{[\mathrm{Cr}] - \\ &(\mathrm{Cr_1}) - K'(\mathrm{Cr_1})^2\} \qquad (6)\end{aligned}$$

The equation can be rearranged to give

$$\begin{aligned}&(\epsilon_{\mathrm{Cr_2}} + \epsilon_{\mathrm{Ce_2}} - \epsilon_{\mathrm{Ce_1Cr_1}})K'(\mathrm{Cr_1})^2 + (\epsilon_{\mathrm{Ce_2}} + \\ &\epsilon_{\mathrm{Cr_1}} - \epsilon_{\mathrm{Ce_1Cr_1}})(\mathrm{Cr_1}) + (\epsilon_{\mathrm{Ce_1Cr_1}} - \epsilon_{\mathrm{Ce_2}})[\mathrm{Cr}] + \\ &\epsilon_{\mathrm{Ce_2}}[\mathrm{Ce}] - D/l + (\epsilon_{\mathrm{Ce_1}} - \epsilon_{\mathrm{Ce_2}})(\mathrm{Ce_1}) = 0 \qquad (7)\end{aligned}$$

At 390 mμ, the observed extinction coefficient of cerium(IV) is constant within experimental error which allows the last term in equation 7 to be dropped since $\epsilon_{\mathrm{Ce_1}} = \epsilon_{\mathrm{Ce_2}}$. If the value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ is known, a simple quadratic equation in $(\mathrm{Cr_1})$ results; all of the other quantities in the equation are known.

In the evaluation of K, one first assumes a value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ and then calculates the values of $(\mathrm{Cr_1})$ using equation 7. Equations 2 and 3 are then used to calculate $(\mathrm{Cr_2})$ and $(\mathrm{Ce_1Cr_1})$. The concentration of uncomplexed cerium(IV), which is equal to the difference between [Ce] and $(\mathrm{Ce_1Cr_1})$, leads, by the method previously outlined,[9] to the values of $(\mathrm{Ce_1})$ and $(\mathrm{Ce_2})$. The value of K can then be calculated. If the same value of K were calculated from the optical density of each solution, the particular assumed value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ leading to this value of K would be considered to be correct as would be that particular K value. Actually it is not possible to find a value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ which leads to exactly the same value of K for every solution. The primary cause is, of course, the experimental error in the determination of the optical density values. The assumed value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ which leads to the values of K with the smallest average deviation from the average value of K is assumed to be the best value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ and the corresponding average value of K is chosen as the best value.

The Estimation of $\epsilon_{\mathrm{Ce_1Cr_1}}$.—The estimation of $\epsilon_{\mathrm{Ce_1Cr_1}}$ would be quite direct if it were possible to measure the light absorption of a solution containing the chromium(VI) present predominantly as the one-to-one complex, the equilibrium in the reaction for its formation having been displaced far to the right by the presence of a large excess of cerium(IV). It is not possible to do this, however; the concentration of cerium(IV) which is necessary to convert > 99% of the chromium(VI) into the complex is so large that the optical opacity of the solution is greater than can be measured with even the shortest cell length (0.1 cm.) which was used in this work. The observed optical density value of the solution of series f (Table I) leads to 2.72×10^3 as the first approximation of the value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ at 390 mμ. This is a lower limit since the chromium(VI) is not completely in the form of the complex in this solution.

The Extinction Coefficient of Cerium(IV).—Earlier studies[6b,c] have shown that cerium(IV) in perchloric acid solution does not obey Beer's law, the failure becoming more pronounced as the wave length is changed from 440 to 530 mμ.[6c] The treatment of the present data to yield the value of K requires the values of $\epsilon_{\mathrm{Ce_1}}$ and $\epsilon_{\mathrm{Ce_2}}$ at the wave lengths of interest. These wave lengths, which were chosen to coincide with the wave length region already studied for chromium(VI),[7b] were not included in the earlier studies[6c] and therefore optical density measurements on solutions of cerium(IV) in 1 M perchloric acid have been made at wave lengths from 370 to 420 mμ. Two series of solutions were studied. In one series, a relatively narrow range of cerium(IV) concentration existed (2.4×10^{-3} to 4.7×10^{-3} gram atom per liter), while in the other series this range was greater (1.4×10^{-3} to 4.7×10^{-2} gram atom per liter). The series with the larger concentration range provided the more stringent test of Beer's law and yielded interesting results. At 420, 410 and 400 mμ, $\epsilon_{\mathrm{Ce_1}} > \epsilon_{\mathrm{Ce_2}}$, while at 380 and 370 mμ, $\epsilon_{\mathrm{Ce_2}} > \epsilon_{\mathrm{Ce_1}}$. At 390 mμ, Beer's law is obeyed within the limits of the experimental error; an average value of ϵ_{Ce} was calculated to be 203, with the average deviation of the 10 individual values from this average value being 0.5%. The average values of the extinction coefficient of cerium(IV) at 390 mμ obtained in the two series differ by 1%; since a similar difference exists between the values of the extinction coefficients calculated for the other wave lengths at comparable concentrations in the two series, it is believed that a slight change in the wave length setting of the instrument may have occurred during the year interval which elapsed between these two series of measurements. The solutions containing both cerium(IV) and chromium(VI) were studied at the same time as the less extensive series of measurements of the extinction coefficient of cerium(IV). The value of the extinction coefficient of cerium(IV) at 390 mμ determined in the less extensive series of measurements was used in the calculations. The data from both series and the value of K''[6a] have been used to calculate $\epsilon_{\mathrm{Ce_1}}$ and $\epsilon_{\mathrm{Ce_2}}$ at the other wave lengths. The extinction coefficients used in the calculations are summarized in Table III.

TABLE III

SUMMARY OF EXTINCTION COEFFICIENT VALUES

Medium, 1.00 M $HClO_4$; temperature 25.0 ± 0.2°

	Wave length, in mμ			
	370	380	390	400
$\epsilon_{\mathrm{Cr_1}}^{7b}$	1016	725	472	297
$\epsilon_{\mathrm{Cr_2}}^{7b}$	2140	2080	1740	1160
$\epsilon_{\mathrm{Ce_1}} \times 10^{-1}$	35[a]	27[a]	20.1	15[a]
$\epsilon_{\mathrm{Ce_2}} \times 10^{-1}$	44[a]	30[a]	20.1	13[a]
$\epsilon_{\mathrm{Ce_1Cr_1}} \times 10^{-2}$	31	31	27.8	22

[a] In the evaluation of these extinction coefficients, a value of K'' of 100[6a] was used; because of the concentration convention used (see Table II), this value is two times the value given in reference 6a.

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(8) The values for the cerium(IV) species are only approximate. In addition to the data from reference 6, the data of M. S. Sherrill, C. B. King and R. C. Spooner (THIS JOURNAL, **65**, 170 (1943)) were used in the estimation of these quantities.

(9) Footnote 8 of reference 7b.

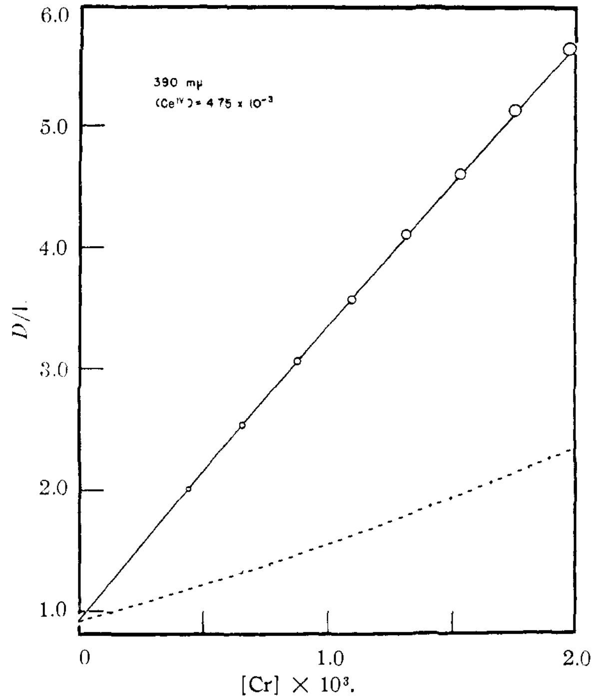

Fig. 1.—D/l *vs.* [Cr] × 10^3: the circles are experimental values with radii corresponding to 1% on the D/l scale. The dashed line gives the expected values if no complexing occurred and the solid line was calculated using the parameters derived in this work; 390 mμ; $(\mathrm{Ce^{IV}}) = 4.75 \times 10^{-3}$.

The Value of K.—Using the observed optical density values at 390 mμ for the 27 solutions of series a-d (Table I), calculations have been made with five different assumed values of $\epsilon_{\mathrm{Ce_1Cr_1}}$. The results of these calculations are summarized in Table IV. It is necessary to mention, however, that the six solutions with the highest concentrations of chromium(VI) yielded K values which were low; these solutions, of all the ones studied, are those in which a complex involving one cerium(IV) and two chromium(VI) atoms would be present to the greatest extent. If the extinction coefficient of this complex ion were less than that of the 1:1 complex ion, the observed trend would be rationalized. If these six solutions are not considered in the calculation, the assumed value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ of 2783 still leads to the smallest deviation (6.4%) of the individual K values from the average K value (3.7×10^3). It is felt, however, that the data are not extensive enough to warrant an attempt to calculate the value of the apparent equilibrium quotient for the formation of the complex containing one cerium(IV) and two chromium(VI) atoms. Therefore, the best value of K will be taken as 3.5×10^3 even though the data suggest that some of the solutions used in arriving at this K value contain significant amounts of higher complexes.

Table IV

Summary of Calculations at 390 mμ

1.00 M $HClO_4$, 25.0 ± 0.2°

Assumed $\epsilon_{\mathrm{Ce_1Cr_1}}$	Average K × 10^{-3}	Average percentage difference between individual values of K and the average value of K
2725	4.5	15
2755	3.9	11.8
2783	3.5	11.5
2810	3.1	12.1
2864	2.7	14

The significance of this K value should again be mentioned. It gives a quantitative description of the complex ion formation between cerium(IV) and chromium(VI) in 1 M perchloric acid even though the monomeric cerium(IV), the monomeric chromium(VI), and possibly the 1:1 complex all exist in that medium in more than one form. The medium was relatively constant since the contribution of cerium(IV) and chromium(VI) to the ionic strength was less than 0.04 M.

The results of the experiments of series d are presented in Fig. 1. It is seen that there is good agreement between the calculated and observed values of D/l.

The Use of the Data at 370, 380 and 400 mμ.—Since at the wave lengths 370, 380 and 400 mμ, the value of $\epsilon_{\mathrm{Ce_1}}$ does not equal the value of $\epsilon_{\mathrm{Ce_2}}$, the calculation of K from the optical density data is more complicated than is the case at 390 mμ. The data obtained at wave lengths other than 390 mμ have been used in a different way. With the value of $K = 3.5 \times 10^3$, the composition of each solution has been calculated by a method of successive approximations. The contribution to the absorption by all of the species except the complex was calculated and was subtracted from the observed absorption. The residual absorption was ascribed to the complex and, having calculated the concentration of the complex, it was possible to calculate the value of $\epsilon_{\mathrm{Ce_1Cr_1}}$. The average value so calculated at each wave length was taken as the value of $\epsilon_{\mathrm{Ce_1Cr_1}}$ at that wave length. These values are presented in Table III. The average percentage differences between the individual calculated values of $\epsilon_{\mathrm{Ce_1Cr_1}}$ for the 27 solutions and the average values were 1.3, 1.3 and 1.5% at 370, 380 and 400 mμ.

A Comparison of the Observed and Calculated Values of D/l.—With the values of $\epsilon_{\mathrm{Ce_1Cr_1}}$ at the several wave lengths and the calculated concentrations of all of the species in each solution, it is possible to calculate a value of D/l for each solution. A measure of the validity of the parameters used is the agreement between these calculated values and the observed values. In addition to the 27 solutions used in the evaluation of K and $\epsilon_{\mathrm{Ce_1Cr_1}}$, the 7 additional solutions (series e and f) were included in this calculation. With the parameters summarized in Table III and a K value of 3.5×10^3, the average percentage difference between the observed and calculated values of D/l was 0.9%.

Experimental Details.—The techniques, equipment and reagents were all the same as described in a previous communication.[7b] All experiments were carried out at 25.0 ± 0.2°. In addition to the reagents used in the previous work,[7b] G. F. Smith reagent grade cerium(IV) perchlorate in 6 M perchloric acid was used as the source of cerium(IV). Since this reagent contained some cerium(III), the solutions which were studied contained cerium(III) at the concentrations shown in Table I.

Discussion

Although the present work is believed to be the first quantitative study of a complex ion equilibrium involving chromium(VI) anionic species and a metal ion, the lack of such data does not appear to be due to the instability of such complexes. In the discussion of certain properties (*e.g.*, solubility), metal chromates and metal sulfates are compared. Many metal ions form sulfate complexes,[10] and the relative basicity of chromate ion compared to sulfate ion is such[7a,b] to suggest that chromate ion has a greater tendency to form complex ions than does sulfate ion. A direct comparison between the stability of the cerium(IV)–chromium(VI) complex ion and the cerium(IV)–sulfate complex ion is meaningful only if these two complex ions have analogous formulas. The cerium(IV)–sulfate complex ions are believed to involve sulfate ion and not bisulfate ion.[11] Since $HCrO_4^-$ is a much weaker acid than HSO_4^-,[12] the cerium(IV) is re-

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(10) Many data are summarized in: R. A. Whiteker and N. Davidson, This Journal, **75**, 3081 (1953).

(11) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951); since the $SO_4^{=}$ concentration, at which there is a lack of dependence of the optical density upon the HSO_4^- concentration, is not stated, it is not known which of the cerium(IV) sulfate complex ions is predominant in the medium. It is possible, of course, that some, but not all, of the sulfate ions which associate with cerium(IV) are present as HSO_4^-.

(12) These acid strengths are discussed in reference 7b.

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 10^8 (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

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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.

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(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).