[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Rates of Water Oxidation in Ceric Perchlorate Solutions[1]

BY DON KOLP[2] AND HENRY C. THOMAS[3]

The oxidation of water by cerium(IV) in perchloric acid solutions has been observed and investigated by several workers.[4-7] In their communication Heidt and Smith[7] propose a mechanism which accounts for their results on the photochemical reduction of cerium(IV) by water. Weiss and Porret[5] as well as Heidt and Smith observed that the reaction is retarded by the presence of cerium(III). The present work was undertaken only incidental to a study of the oxidation of formic acid in perchloric acid solutions of cerium(IV) and does not constitute an exhaustive investigation of the water reaction. However, the effect of the concentration of cerium(III) has been the object of particular study. We are concerned here with the thermal reaction; excitation by ultraviolet radiation was not present.

Experimental

Eighteen solutions of mixed ceric and cerous perchlorate were used. The perchlorate solutions were near 3.6, 5.4 and 7.4 molar. Cerium(IV) concentrations varied from 0.1 to 0.4 molar in two steps; cerium(III) concentrations, from 0.1 to 0.3 molar in two steps. (All concentrations mentioned in this section and in the section on results are to be understood as analytical concentrations, in volume formal units, and will be designated by *M*.)

The solutions were prepared as follows. "Reference" grade ammonium hexanitratocerate, stated by the manufacturer (the G. Frederick Smith Chemical Co.) to be 100.0% pure, in amount 1.2 moles, was dissolved in a minimum quantity of distilled water. This solution was added slowly with vigorous stirring to twice the equivalent amount of 3% ammonia solution. After the heavy precipitate of ceric hydroxide had settled, the liquid was decanted and the precipitate transferred to a Buchner funnel fitted with a circle of hardened paper. The precipitate was washed about twenty times on the filter, the final washings giving a negative test for ammonia. The precipitate was divided into three nearly equal parts. One portion was dissolved in 670 ml. of "Baker's Analyzed" perchloric acid, another, in 500 ml., and the third, in 330 ml. of the acid. These solutions were filtered through sintered glass, and each was diluted to a volume of one liter. The three solutions were approximately 0.4 *M* in cerium(IV). Solutions approximately 0.1 and 0.2 *M* in ceric cerium were prepared by dilution with appropriate acid. Six additional solutions were thus prepared.

Solutions containing cerium(III) were prepared from the 0.2 and 0.4 *M* cerium(IV) solutions by reduction of a portion with a few drops of 30% hydrogen peroxide and subsequent addition of a similar volume of the parent solution: Of the solutions thus produced those with cerium(IV) concentrations of 0.2 *M* were further partially reduced. These operations produced nine additional solutions.

The eighteen solutions were analyzed for total cerium by the method of Willard and Young.[8] The perchloric acid was removed by evaporation with sulfuric acid to fumes of sulfur trioxide before oxidation with ammonium persulfate. Titrations were made with recently standardized ferrous ammonium sulfate solution. This solution was standardized against a ceric sulfate solution which had been standardized by weight against Bureau of Standards sodium oxalate. Duplicate determinations of total cerium agreed to 0.1%.

The perchlorate content of each of the eighteen solutions was determined by the method of V. Rothmund.[9] The excess titanous sulfate was destroyed with an equivalent amount of potassium permanganate. Chloride was determined in the resulting solutions by the Volhard titration. A blank determination was carried out on the reagents, the results of which were applied to the data. Duplicate determinations agreed to 0.2%.

If the cerium hydroxide precipitate contained no bases other than $Ce(OH)_4$ and $Ce(OH)_3$, the available hydrogen ion content of the solution resulting when the precipitate was dissolved in perchloric acid is given by $(H^+) = (ClO_4) - 3(CeIII)\text{-}4(Ce(IV))$. This formula will continue to hold when a part of the Ce(IV) is reduced to Ce(III) because one hydrogen ion is liberated in the reduction of each Ce(IV), whether the reduction be accomplished by water or by hydrogen peroxide. Thus the hydrogen ion concentrations of the solutions may be calculated from the analytical data on perchlorate and cerium.

The rate measurements were carried out as follows. For a single series twelve 13 × 100 mm. test-tubes were cleaned by heating in dichromate–sulfuric acid solution, rinsing ten times with tap water and five times with distilled water. The tubes were dried and a 5-ml. portion of the solution to be studied was sealed into each. The tubes were placed in a thermostat and allowed two to five hours to reach temperature equilibrium. To determine the initial cerium(IV) concentration, a tube was opened and emptied into a flask, previously weighed with its contents, containing 25 ml. of cool 2 *M* sulfuric acid. The reaction was stopped by this dilution in sulfuric acid. The flask was again weighed and the cerium(IV) determined by titration with ferrous solution, using ferroin as the indicator. Because of some fading of the end-point these titrations are subject to an error of ±0.3%. The initial concentration of cerium(III) follows from the known total cerium content of the solution. The remaining samples were titrated by the same procedure at intervals of one or two days. The time at which each sample was stopped was observed with an uncertainty of no more than a minute.

The densities of the reaction mixtures were determined pycnometrically at the temperatures of the rate measurements. They were found to change less than 0.1% as the reaction proceeded.

Results

Eighteen runs were made at 60.0°. Three runs each were made at 45.0 and 30.0°. The results were much more consistent at the highest temperature. In Table I the complete data are given for a single run at 60.0°. The entries are self-explanatory with the exception of those in the fifth and sixth columns, which were arrived at as follows.

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[1] This paper is based upon the dissertation presented by Don Kolp in 1948 to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The material of this paper was presented in part at the 115th National Meeting of the American Chemical Society in San Francisco, California.

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[4] E. Bauer, *Z. physik. Chem.*, **63**, 683 (1908).

[5] J. Weiss and D. Porret, *Nature*, **139**, 1019 (1917).

[6] G. F. Smith, "Cerate Oxidimetry," G. F. Smith Co., Columbus, Ohio, pp. 93–95.

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

[8] H. H. Willard and P. Young, THIS JOURNAL, **50**, 1379 (1928).

[9] V. Rothmund, *Z. anorg. Chem.*, **62**, 108 (1909).

An empirical differential equation has been found which correlates all of the results in a satisfactory manner. Writing C_4 and C_3 for the analytical concentrations of cerium(IV) and cerium(III), this equation is

$$\frac{dC_3}{dt} = k_e \frac{C_4^{5/3}}{C_3} \tag{1}$$

at fixed perchlorate concentration and at fixed temperature. On integration this equation gives the relation

$$f \equiv \frac{3(C_4 + C_3)}{2C_4^{2/3}} + 3C_4^{1/3} = k_e t + f_0 \tag{2}$$

where f_0 is the value of the left side of the equation at the time ($t = 0$) of the first analysis of a series. The computed values of $f - f_0$ according to (2) are given in the fifth column of Table I and the corresponding values of k_e in the sixth. The linearity with time of $f - f_0$ is evident. The results at 60° are all reasonably well represented by such straight lines. The data at the lower temperatures are much less precise. Table II gives the initial conditions for the various series and the values of k_e as graphically determined. At 30° these slopes can be considered only rough approximations.

The experimental results are summarized in the following empirical equations for the constants k_e of equation (1). Variation with total perchlorate content at fixed temperature

60° $\log k_e = 0.116[\mathrm{ClO_4}] - 4.29$
45° $\log k_e = 0.238[\mathrm{ClO_4}] - 6.19$
30° $\log k_e = 0.218[\mathrm{ClO_4}] - 7.08$

Variation with temperature at fixed total perchlorate content

$7.50M$ $\mathrm{ClO_4}$ $\log k_e = 16.7 - 6700/T$
$5.25M$ $\mathrm{ClO_4}$ $\log k_e = 20.5 - 8100/T$
$3.75M$ $\mathrm{ClO_4}$ $\log k_e = 25.8 - 9900/T$

Since the total perchlorate content of the solutions does not vary during the course of the reaction, it, rather than the perchloric acid content, has been selected as the basis for the correlation of the data.[10] These equations are not to be taken as implying the independence of the reaction rate and hydrogen ion concentration. They are only summaries of the experimental results under the conditions given in Table II.

Discussion

A possible interpretation of the empirical differential equation (1) is afforded by the mechanism proposed by Heidt and Smith[7] for the photochemically excited oxidation of water by cerium (IV). For our case, in which only thermal excitation is present, their mechanism is represented by the equations

$$\begin{array}{ll}
2C_m \rightleftarrows C_p & K \\
C_p \longrightarrow C_p^* & k_1 \\
C_p^* + H_2O \longrightarrow 2C_3 + 2H^+ + {}^1/{}_2O_2 & k_2 = k_2'[H_2O] \\
C_p^* + C_3 \longrightarrow C_p + C_3 & k_3 \\
C_p^* + S \longrightarrow C_p + S & k_4 = k_4'[S]
\end{array}$$

The oxidation is considered to be caused by an energetic dimer, C_p^*, of ceric cerium. The dimerization is supposed to be fast with respect to the remaining reactions. The inhibition of the water oxidation is due to the deactivation of the excited dimer by cerous cerium, C_3; further inhibition by the remainder of the environment, S, is repre-

TABLE I

OXIDATION OF WATER BY CERIC PERCHLORATE AT 60.0°

Total cerium, $0.3794M$; perchlorate, $5.24M$

Time, hours	Ce(IV), moles/liter	Ce(III), moles/liter	H, moles/liter	$f - f_0$, $M^{1/3}$	$k_e \times 10^4$ $M^{1/3}$/hours
0.0	0.1840	0.1954	3.92	0.0000	...
48.5	.1800	.1994	3.92	.0132	2.7
96.0	.1768	.2026	3.93	.0243	2.5
145.1	.1735	.2059	3.93	.0375	2.6
191.8	.1709	.2085	3.93	.0444	2.3
263.9	.1662	.2132	3.94	.0663	2.5
312.2	.1641	.2153	2.94	.0753	2.4
432.3	.1577	.2217	3.95	.1050	2.4
503.8	.1544	.2250	3.95	.1212	2.4
599.7	.1506	.2288	3.95	.1413	2.4

TABLE II

OXIDATION OF WATER BY CERIC PERCHLORATE

$\mathrm{ClO_4}$, moles/liter	Total Ce, moles/liter	Initial Ce(IV), moles/liter	$k_e \times 10^4$, $M^{1/3}$/hours
	(A) 60.0°		
7.36	0.3776	0.3393	3.5
7.43	.1887	.1572	3.7
7.46	.0919	.0731	3.5
7.22	.3712	.1838	3.7
7.26	.1833	.0876	3.7
7.16	.3683	.0830	3.3
5.28	.3849	.3556	2.0
5.49	.1913	.1606	2.2
5.45	.0945	.0759	2.2
5.24	.3794	.1840	2.3
5.41	.1885	.0947	2.4
5.22	.3776	.0956	1.7
3.54	.3776	.3534	0.79
3.72	.1880	.1680	1.3
3.76	.0961	.0755	1.2
3.48	.3739	.1786	1.2
3.67	.1857	.0838	1.5
3.50	.3694	.0915	1.6
	(B) 45.0°		
			$k_e \times 10^5$
7.44	0.3817	0.3556	3.8
5.43	.3892	.3651	1.2
3.57	.3813	.3596	0.45
	(C) 30.0°		
			$k_e \times 10^7$
7.52	0.3859	0.3612	5.9
5.39	.3929	.3689	20
3.61	.3849	.3615	2.6

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[10] In the abstract of this paper published for the 115th National Meeting of the American Chemical Society these equations were erroneously given in terms of perchloric acid content. Here also the constant for the temperature variation at 7.50 M $\mathrm{ClO_4}$ was given as 17.7 instead of 16.7.

sented by the last equation. If we write $T = 2C_p + \sqrt{C_p/K}$ for the total Ce(IV) content of the solution, neglecting C_p^* as compared to the bulk of the Ce(IV), the usual steady state approximation immediately produces the rate equation

$$-\frac{dT}{dt} = \frac{kC_p}{m + C_3} \qquad (4)$$

where $k = 2k_1k_2/k_3$ and $m = (k_2 + k_4)/k_3$. For convenience we select $z = \sqrt{C_p/K}$ as the dependent variable and integrate (4) with the result

$$F \equiv \frac{M}{Kz} + \left(\frac{1}{K} - 4M\right) \ln z + 6z + 4Kz^2 = kt + F_0 \qquad (5)$$

In this equation $M = m + a + b$, a and b being the initial total Ce(IV) and Ce(III) concentrations, respectively. In equation (5) we have a means of representing the rate data in terms of the equilibrium constant of the dimerization and the group of constants m. Unfortunately there are not available independent determinations of these constants, hence the application of (5) to the data of this paper can be considered only tentative. Comparison of the empirical equation (1) and equation (4) indicates that m is probably small with respect to C_3 and hence with respect to $a + b$. As a preliminary test of (5) we thus put $M \simeq a + b$. We now have an equation with one adjustable constant, K. The data on the water oxidation at 60° can be well represented by this equation with reasonable values of K. If one chooses $K = 1.0$ and applies (5) to a run with $[ClO_4] = 7.16$, $a = 0.0830$, $b = 0.2853$, the values of $F - F_0$ fall close to a straight line with slope $k = 1.15 \times 10^{-3}$. Using the same value of K in a run with nearly the same perchlorate concentration, $[ClO_4] = 7.43$, and a widely different ratio of initial concentrations, $a = 0.1572$ and $b = 0.0315$, the straight line through the points has the slope $k = 1.17 \times 10^{-3}$. Since the only criterion for the correct choice of K is the fit of the data to a straight line, considerable latitude in the choice of K is permissible. About the most that can be said is that higher values of K must be chosen for lower perchloric acid concentrations. Thus at $[ClO_4] = 3.72$, K must be chosen in the range 2.0 to 2.5. It will be necessary to test the mechanism using independent determinations of the dimerization constants. A further interesting study will be the comparison of the rate of the deactivation reaction, given by k_3, with the rate of the electron exchange reaction between ceric and cerous cerium.

Summary

1. Rate data are presented on the thermal reaction in perchloric acid solution between ceric cerium and water. Empirical equations summarizing these data are reported.

2. The results are examined in the light of the mechanism of Heidt and Smith for this reaction. The data are shown to be consistent with this mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Chlorination of Bicyclo[2,2,1]heptane (Norbornylane)

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The nitration of bicyclo[2,2,1]heptane (norbornylane[3]) has been reported to give 1-nitrobicyclo[2,2,1]heptane.[4] In the present investigation a study was made of the peroxide-catalyzed chlorination of bicyclo[2,2,1]heptane with sulfuryl chloride[5] in an attempt to find a convenient synthesis for the 1- and 7-chlorobicyclo[2,2,1]-heptanes. Both mono- and dichloro products were isolated from the chlorination of bicyclo-[2,2,1]heptane in methylene chloride solution. The monochloride fraction had practically the same physical properties (Table I) and infrared absorption spectrum (Fig. 1) as a sample of norbornyl chloride (2-chlorobicyclo[2,2,1]heptane) made by the addition of hydrogen chloride to norbornylene (bicyclo[2,2,1]2-heptene).[6]

TABLE I

PHYSICAL PROPERTIES AND SOLVOLYTIC RATE CONSTANTS

Chloride	B. p., °C.	Mm.	M. p., °C.	$n^{25}D$	d^{25}_4	k_1,[a] hr.$^{-1}$
Product of addition of hydrogen chloride to bicyclo[2,2,1]2-heptene	97	100	-6[b]	1.4823	1.060	0.151
Product from the chlorination of bicyclo[2,2,1]-heptane	88–89	74	..	1.4824	1.061	.152
Chlorination of bicyclo-[2,2,1]heptane (after partial hydrolysis)	79	46	-4[b]	1.4825	1.059	.116
Cyclopentyl chloride	...	...	..	....	...	.017

[a] Solvolysis rate constant for aqueous alcohol (80% ethanol and 20% water by volume) at 85°. [b] Melting point of a mixture of approximately equal weights of these materials was −5°.

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[3] Bicyclo[2,2,1]heptane and its derivatives are listed by *Chemical Abstracts* as "norcamphanes." In this paper the more desirable name, norbornylane, is used for the parent hydrocarbon; *cf.* Komppa and Beckmann [*Ann.*, **512**, 172 (1934)].

[4] Blickenstaff and Hass, THIS JOURNAL, **68**, 1431 (1946).

[5] Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

[6] Schmerling, *ibid.*, **68**, 195 (1946).