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# The Kinetics and Mechanism of the Reaction of Cerium(IV) and Chromium(III)[1,2]

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In acidic aqueous sulfate media, the rate law for the oxidation of chromium(III) by cerium(IV) has been found to be $d[Cr^{VI}]/dt = k[Ce^{IV}]^2[Cr^{III}]/[Ce^{III}]$. This rate law indicates that the transition state for the reaction contains one cerium atom and one chromium atom with an average oxidation state for the two metal atoms of + 4. A reasonable mechanism consistent with this involves a rate-determining reaction of cerium(IV) with chromium(IV), the concentration of which is determined in a relatively rapid equilibrium with chromium(III), cerium(IV) and cerium(III). The empirical rate coefficient $k$ shows an approximately inverse square dependence upon the concentration of bisulfate ion.

The role of the relatively unstable + 4 and + 5 oxidation states of chromium in oxidation-reduction reactions is of interest. The reaction of the three-equivalent oxidizing agent chromium(VI) and the one-equivalent reducing agent iron(II) is second order in iron(II) and is retarded by iron(III) thus suggesting the one-equivalent reaction step involving iron(II) and chromium(V) to be rate-determining.[4,5a,6] Reactions induced by the reaction of chromium(VI) and various reducing agents demonstrate both chromium(IV) and chromium(V) as possible reaction intermediates.[5] These relatively unstable oxidation states are also undoubtedly present as reaction intermediates in the reaction of chromium(III) and the relatively powerful oxidizing agents which are capable of oxidizing chromium(III) in acidic solution. Cerium(IV) is such an oxidizing agent, and although the cerium(IV)-chromium(III) reaction has been used in analysis,[7] the kinetics of this reaction have not been investigated. In the present study, the rate of this reaction

$$3Ce^{IV} + Cr^{III} = 3Ce^{III} + Cr^{VI}$$

has been determined at 25.0° in aqueous acidic solutions containing sulfate. The rate of reaction is conveniently measurable in such solutions; it is inconveniently high in perchloric acid solution. Sulfate-containing reaction media are not without complexities; complex ions involving sulfate and cerium(IV),[8] cerium(III)[9] and chromium(III)[10] exist. The sulfate complexes of cerium(IV) and cerium(III) and the outer-sphere complex of sulfate and hexaaquochromium(III) ion are in rapid equilibrium with their environment. This is not true of the inert chromium(III) sulfate inner-sphere complexes, which apparently do not form to a significant extent during the course of a kinetic run. The interpretation of kinetic studies in solutions of varying concentrations of cerium(IV), cerium(III) and chromium(III) but constant sulfate ion concentration is not complicated by these sulfate complex ion equilibria.

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[1] Taken from the Ph.D. thesis of James Y.-P. Tong, University of Wisconsin, 1953. Presented at 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958.

[2] This work was supported in part by a grant from the U. S. Atomic Energy Commission (Contract AT(11-1)-64, Project No. 3).

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[4] (a) C. Benson, *J. Phys. Chem.*, **7**, 1, 356 (1903); (b) C. Wagner and W. Preiss, *Z. anorg. Chem.*, **168**, 265 (1928); (c) C. Wagner, *ibid.*, **168**, 279 (1928).

[5] (a) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949); (b) I. M. Kolthoff and M. A. Fineman, *J. Phys. Chem.*, **60**, 1383 (1956); (c) W. A. Waters, *Quart. Revs.*, **12**, 277 (1958).

[6] The use of the term three-equivalent oxidizing agent follows the suggestion of W. C. E. Higginson and J. W. Marshall (*J. Chem. Soc.*, 447 (1957)); its superiority to the term three-electron oxidizing agent lies in the fact that it does not suggest electron transfer as the reaction mechanism.

[7] H. H. Willard and P. Young, THIS JOURNAL, **51**, 139 (1929).

[8] T. J. Hardwicke and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

[9] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

[10] (a) Outer-sphere complexes, R. E. Connick and M.-S. Tsao, Paper No. 9, Division of Physical and Inorganic Chem., 123rd National A. C. S. Meeting, Los Angeles, March, 1953. (b) Inner-sphere complexes, reference 1, and N. Fogel and J. M. J. Chow, Paper No. 96, Division of Inorg. Chem., 136th National A. C. S. Meeting, Atlantic City, Sept., 1959.

## Experimental Details

**Reagents.**—Chromium(III) perchlorate was prepared by the reaction of chromium trioxide with hydrogen peroxide in perchloric acid solution. Following the reaction, chromium(III) perchlorate was crystallized from solution and then recrystallized from 1 *M* perchloric acid.

Two independent sources of cerium(IV) were used. One was reagent grade cerium(IV) perchlorate in 6 *M* perchloric acid (G. F. Smith Chemical Company); the other was a cerium(III)–cerium(IV) solution prepared by the electrolytic oxidation of cerium(III) sulfate in sulfuric acid.

Cerium(III) perchlorate was prepared from $(NH_4)_2Ce(NO_3)_6$ by first converting it to a solution of cerium(III) chloride in hydrochloric acid, next extracting this solution with isopropyl ether to remove any iron which might have been present and then precipitating cerium(III) chloride by saturation of the solution with hydrogen chloride. The cerium(III) chloride was converted to cerium(III) perchlorate by fuming with perchloric acid; if the resulting solution showed any coloration due to the presence of cerium(IV), it was reduced with an equivalent amount of hydrogen peroxide. Cerium(III) perchlorate was precipitated from the solution by chilling.

Ammonium perchlorate solution was prepared by the reaction of ammonium hydroxide and perchloric acid. Sodium perchlorate solution was prepared by the reaction of sodium carbonate and perchloric acid.

The chemical substances used in the above described preparations as well as all other chemical substances used in this work were of reagent grade quality.

Doubly distilled water was used in the preparation of all solutions; the second distillation was from alkaline permanganate solution using a Barnstead still.

**The Reaction Media.**—The reaction was carried out in media of varying concentration of ammonium ion, hydrogen ion, sulfate ion and bisulfate ion. A value of the bisulfate ion acid dissociation equilibrium quotient $Q_2 = [H^+][SO_4^=]/[HSO_4^-] = 0.42$ was used in planning the composition of the solutions; all solutions have an ionic strength $I = 2.35$ *M*.[11] The compositions of the five different reaction media are given in Table I. The maximum initial concentrations of the reagents not listed in Table I are cerium(IV), 0.023 *M*; cerium(III), 0.055 *M*; and chromium(III), 0.042 *M*. It was assumed that the presence of these substances did not alter the medium in the sense that the appropriate activity coefficients were not changed with a variation in their concentrations. This latter assumption, upon which the derivation of the reaction orders with respect to chromium(III), cerium(IV) and cerium(III) depends, is probably more nearly correct than is the assumption that $Q_2$ has the same value in each of the five media of ionic strength 2.35 *M*. Only the determination of the reaction order with respect to sulfate ion and hydrogen ion depend upon the assumed constancy of $Q_2$.

TABLE I

REACTION MEDIA[a]

$I = 2.35\ M \qquad Q_2 = \frac{[H^+][HSO_4^-]}{[HSO_4]} = 0.42$

| | Stoichiometric concentrations | | | Calculated concentrations | | |
|---|---|---|---|---|---|---|
| Series | $C_{HClO_4}$ | $C_{NaClO_4}$ | $C_{(NH_4)_2SO_4}$ | $[H^+]$ | $[SO_4^=]$ | $[HSO_4^-]$ |
| 1 | 1.652 | ... | 0.464 | 1.30 | 0.11 | 0.35 |
| 2 | 0.522 | ... | .800 | 0.24 | .51 | .39 |
| 3 | 1.350 | 0.372 | .400 | 1.06 | .11 | .29 |
| 4 | 1.279 | .599 | .301 | 1.06 | .086 | .22 |
| 5 | 1.207 | .829 | .200 | 1.06 | .057 | .14 |

[a] A formula in brackets denotes the molar concentration of the indicated species. The quantity $C_{XY}$ denotes the stoichiometric molarity of XY.

**The Kinetic Runs.**—The kinetic runs were conducted by rapidly mixing thermostated stock solutions and then transferring the mixture to the appropriate spectrophotometer cell. (Cells of 1, 2, 5 and 10 cm. length were used.) A Beckman Model DU Spectrophotometer with a thermostated cell compartment was used for the absorbancy measurements; the measured absorbancy values were in the range 0.2 to 0.8. The initial absorbancy measurement was generally made 2–4 minutes after mixing; as many as 50 absorbancy measurements were then made at 0.5 to 10 minute intervals for a period of 30 to 150 minutes.

**The Absorbancy Indices.**—The absorbancy values of reaction mixtures have been followed at 492 and 500 mμ; at these wave lengths, only cerium(III), among the reactant and product species, is transparent. The absorbancy indices of cerium(IV), chromium(III) and chromium(VI) have been determined at these wave lengths in each of the reaction media. Outer-sphere complexing of chromium(III) generally manifests itself in the ultraviolet region of the spectrum but not in the visible region.[12] This was confirmed, at least approximately; the values of the absorbancy indices of hexaaquochromium(III) ion at 492 and 500 mμ are 3.58 ± 0.06 and 4.21 ± 0.07, respectively; the uncertainties listed are the average of the differences between the average value obtained for all media and the average values obtained for each medium. The values of the other relevant absorbancy indices are given in Table II. These absorbancy indices were measured on solutions with a five- to ten-fold range of concentration of the absorbing substance; Beer's law was obeyed in all cases. This, at first sight, may seem surprising since both cerium(IV) and chromium(VI) can exist as monomeric and dimeric species. In the case of cerium(IV), the dimerization is suppressed by the high concentration of sulfate which converts the cerium(IV) very predominantly to sulfate (and/or bisulfate) complexes.[8] In the case of chromium(VI), the monomer and dimer have approximately equal absorbancy indices (per gram atom of chromium(VI)) at these wave lengths.[13]

TABLE II

THE ABSORBANCY INDICES OF CERIUM(IV) AND CHROMIUM (VI) IN THE REACTION MEDIA, $T = 25.0°$

| Medium for series no. | Cerium(IV) | | Chromium(VI) | |
|---|---|---|---|---|
| | 492 mμ | 500 mμ | 492 mμ | 500 mμ |
| 1 | $14.0_4$ | 9.18 | 82.3 | 61.1 |
| 2 | 10.1 | 6.39 | 79.2 | 57.8 |
| 3 | $13.3_4$ | 8.71 | 81.6 | 60.6 |
| 4 | 13.9 | 9.11 | (80.5)[a] | (59.4)[a] |
| 5 | 14.4 | 9.51 | 79.3 | 58.1 |

[a] Obtained by interpolation.

## Experimental Results

The concentration of chromium(VI), in gram atoms per liter, at a particular time was obtained from the absorbancy reading at that time by the use of an equation derivable from the reaction stoichiometry

$$[Cr^{VI}] = \{A - A_0\}/b(a_{VI} - a_{III} - 3a_{IV}) \quad (1)$$

in which $A$ and $A_0$ are the absorbancy values at the time under consideration and at zero time, respectively, $b$ is the cell length and $a_{VI}$, $a_{III}$ and $a_{IV}$ are the absorbancy indices of chromium(VI), chromium(III) and cerium(IV).[14] The value of $d[Cr^{VI}]/dt$ is, therefore, directly proportional to $dA/dt$. The quantity $(a_{VI} - a_{III} - 3a_{IV})$ was obtained by subtracting numbers of comparable magnitude. It must be admitted, therefore, that the values of the reaction rate obtained were not highly accurate; in the original treatment of the data the values of $dA/dt$ were obtained analytically

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[11] The value of $Q_2$ at $I = 2.35$ *M* was obtained by interpolation of the equilibrium quotient values obtained from the study of Raman spectra of ammonium bisulfate solutions: T. F. Young, L. F. Maranville and H. M. Smith, Chap. IV of "The Structure of Electrolytic Solutions," Edited by W. J. Hamer, John Wiley and Sons, Inc., New York, New York, 1959. (We are grateful to Professor Young for making these data available to us in 1953.)

[12] This has been demonstrated for the chromium(III)–chloride system; H. S. Gates and E. L. King, THIS JOURNAL, **80**, 5011 (1958).

[13] J. Y.-P. Tong and E. L. King, *ibid.*, **75**, 6180 (1953).

[14] In describing the light absorption measurements, the nomenclature recommended in the National Bureau of Standards Letter Circular LC 857 (1947) is used.

at two to six points in each experiment.[1] The procedure involved the derivative of the Lagrangian interpolation formula and was applied to seven values of $A$ at equally spaced time intervals.[15] The correlation of the values of $\mathrm{d}A/\mathrm{d}t$, with the concentrations indicated that the rate law

$$\frac{\mathrm{d}[\mathrm{Cr^{VI}}]}{\mathrm{d}t} = \frac{k[\mathrm{Ce^{IV}}]^2[\mathrm{Cr^{III}}]}{[\mathrm{Ce^{III}}]} \tag{2}$$

was obeyed in each of the reaction media. In this rate law, a symbol in brackets stands for the total concentration of the element in the indicated oxidation state and not the concentration of a particular species. Values of the rate coefficient $k$ were obtained from values of $\mathrm{d}A/\mathrm{d}t$ by the equation

$$k = \frac{[\mathrm{Ce^{III}}]}{[\mathrm{Ce^{IV}}]^2[\mathrm{Cr^{III}}]} \cdot \frac{1}{b(a_{\mathrm{VI}} - a_{\mathrm{III}} - 3a_{\mathrm{IV}})} \cdot \frac{\mathrm{d}A}{\mathrm{d}t} \tag{3}$$

In the series of experiments in reaction medium no. 2, the value of $k$ calculated in this way over a ~20-fold variation in $[\mathrm{Ce^{IV}}]/[\mathrm{Ce^{III}}]$ (from ~0.2 to ~4) varies by 40–50%. Considering that the calculated values of $k$ obtained at a particular value of $[\mathrm{Ce^{IV}}]/[\mathrm{Ce^{III}}]$ vary by a comparable amount, it is clear that the one parameter rate equation is all that the present data really warrant. For the experiments in this series, there is a faint suggestion in the data that the denominator might be $\{[\mathrm{Ce^{III}}] + k'[\mathrm{Ce^{IV}}]\}$; the experiments upon which this conclusion depends are ones in which the concentration of cerium(III) is known least accurately. It can be stated that $k'$ probably is less than ~0.7.

Rather than report the values of $k$ calculated from the values of $\mathrm{d}A/\mathrm{d}t$, it seems preferable to report the values obtained from fitting the data to the integrated rate law. The integration of rate equation 2 by the method of partial fractions yields

$$\begin{aligned} &+ \left\{\frac{3[\mathrm{Cr^{III}}]_0 + [\mathrm{Ce^{III}}]_0}{(3[\mathrm{Cr^{III}}]_0 - [\mathrm{Ce^{IV}}]_0)^2}\right\} \times \ln\left\{\frac{[\mathrm{Ce^{IV}}]}{[\mathrm{Cr^{III}}]}\right\} + \\ &\left\{\frac{[\mathrm{Ce^{III}}]_0 + [\mathrm{Ce^{IV}}]_0}{3[\mathrm{Cr^{III}}]_0 - [\mathrm{Ce^{IV}}]_0}\right\} \times \left\{\frac{1}{[\mathrm{Ce^{IV}}]}\right\} = kt + \\ &\left\{\frac{3[\mathrm{Cr^{III}}]_0 + [\mathrm{Ce^{III}}]_0}{(3[\mathrm{Cr^{III}}]_0 - [\mathrm{Ce^{IV}}]_0)^2}\right\} \times \ln\frac{[\mathrm{Ce^{IV}}]_0}{[\mathrm{Cr^{III}}]_0} + \\ &\left\{\frac{[\mathrm{Ce^{III}}]_0 + [\mathrm{Ce^{IV}}]_0}{3[\mathrm{Cr^{III}}]_0 - [\mathrm{Ce^{IV}}]_0}\right\} \times \left\{\frac{1}{[\mathrm{Ce^{IV}}]_0}\right\} \end{aligned} \tag{4}$$

which has the form

$$y = kt + y_0 \tag{4'}$$

The initial concentrations and the observed values of the absorbancy allow the calculation of both $y$ and $y_0$. All of the data in each run were fit to equation 4′ by the method of least squares with $y_0$ as a parameter to be evaluated. The values of $y_0$ so calculated agreed, with a few exceptions, with the values calculated from the initial composition within a few per cent. The values of $k$ obtained in these calculations, presented in Table III, differ from those derived from the slopes of $A$ *versus* time by an average amount of 4.5%. Although the $k$ values are not as accurately known as might be desired, the concentration ranges studied were so large that one has considerable confidence in the form of the rate law.

The empirical rate coefficient defined by rate equation 2 shows an approximate inverse square dependence upon the concentration of bisulfate ion; the values of the product $k[\mathrm{HSO_4^-}]^2$ for the five reaction media are 0.61, 0.74, 0.49, 0.65 and 0.78 mole$^{-1}$ liter$^{-1}$ sec.$^{-1}$. This dependence is, of course, experimentally indistinguishable from one, $k \propto [\mathrm{H^+}]^{-2}[\mathrm{SO_4^=}]^{-2}$. The uncertainty in the average value of $k$ obtained in each series is so large and the assumption of a constant value of $Q_2$ is so questionable that there is no point in attempting any more elaborate correlation of the values of $k$ with the composition of the medium.

## Discussion

The inverse dependence of the reaction rate upon the concentration of cerium(III), a reaction product, and the second order dependence upon cerium(IV) are the most striking and revealing results of the present study. The retarding action of cerium(III) cannot be due to the reverse of the over-all reaction because the form of the rate law is not of the type resulting from such a cause. The particular type of dependence of reaction rate upon cerium(III) suggests that it is produced in a reaction step which precedes the rate-determining step. The composition of the transition state for this rate-determining step, as revealed by the form of the rate law ($\mathrm{X}^* = 2\,\mathrm{Ce^{IV}} + \mathrm{Cr^{III}} - \mathrm{Ce^{III}}$), contains one cerium atom and one chromium atom, and the *average* oxidation state of the two metal atoms is +4.

A reasonable mechanism for the reaction of the three-equivalent reducing agent chromium(III) and the one-equivalent oxidizing agent cerium(IV) is the sequence of three one-equivalent reactions

$$\mathrm{Ce^{IV} + Cr^{III}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Ce^{III} + Cr^{IV}}$$

$$\mathrm{Ce^{IV} + Cr^{IV}} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{Ce^{III} + Cr^{V}}$$

$$\mathrm{Ce^{IV} + Cr^{V}} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \mathrm{Ce^{III} + Cr^{VI}}$$

The observed rate law is consistent with the second of these reactions being the rate-determining step. The concentration of the unstable intermediate chromium(IV), a reactant in this step, is fixed by

$$[\mathrm{Cr^{IV}}] = k_1[\mathrm{Cr^{III}}][\mathrm{Ce^{IV}}]/k_2[\mathrm{Ce^{III}}]^{16}$$

equilibrium in the first step. The empirical rate coefficient $k$ is, therefore, identified as $k_1k_3/k_2$, and $k'$, which may be barely detectable, is identified as $k_3/k_2$. The observed unimportance of the $k'$ term indicates that $k_2[\mathrm{Ce^{III}}] > k_3[\mathrm{Ce^{IV}}]$. Another consequence of the observed rate law is the inequality $k_5[\mathrm{Ce^{IV}}] >> k_4[\mathrm{Ce^{III}}]$.

That the chromium(IV)–chromium(V) transformation should be the bottleneck in the oxidation of chromium(III) by cerium(IV) is of interest for, as already mentioned, it is this same transformation, in reverse, which appears to be the slow step

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(15) H. E. Salzer, "Table of Coefficients for Obtaining the First Derivative Without Differences," National Bureau of Standards, Applied Mathematics Series (1948).

(16) This reversible first step provides a pathway for the cerium(IV)-catalyzed exchange of oxygen between hexaaquochromium(III) ion and water observed by R. A. Plane and H. Taube (*J. Phys. Chem.*, **56**, 33 (1952)).

TABLE III

EXPERIMENTALLY DETERMINED VALUES OF THE RATE CONSTANTS IN THE SEVERAL REACTION MEDIA

$T = 25 \pm 0.5°$

| Exp.[a, b] | Initial concentrations (× $10^3$ l./mole) | | | Extent of reaction followed (%) | $k$[c] (× $10^3$ $l.^{-1}$ mole sec.) |
|---|---|---|---|---|---|
| | [$Ce^{IV}$] | [$Ce^{III}$] | [$Cr^{III}$] | | |
| 1-1 | 9.30 | 6.94 | 8.71 | 5–42 | 5.5 |
| -2 | 4.65 | 0.033 | 8.71 | 17–63 | 4.8 |
| -3 | 2.79 | 0.020 | 2.18 | 9–48 | 5.7 |
| -4[d] | 0.93 | 0.0066 | 4.35 | 8–50 | 4.0 |
| | | | | | Av. 5.0 ± 0.6 |
| 2-1 | 17.26 | 2.49 | 42.6 | 24–77 | 6.0 |
| -2 | 17.26 | 5.94 | 42.6 | 21–74 | 5.9 |
| -3 | 23.32 | 3.46 | 21.3 | 18–60 | 4.6 |
| -4 | 23.32 | 3.46 | 8.52 | 12–44 | 5.0 |
| -5 | 23.32 | 20.73 | 21.3 | 8–79 | 4.9 |
| -6 | 23.32 | 38.0 | 42.6 | 11–64 | 5.8 |
| -7 | 11.66 | 1.73 | 21.3 | 20–55 | 4.5 |
| -8 | 23.32 | 55.3 | 42.6 | 8–42 | 5.6 |
| -9 | 4.65 | 0.033 | 8.52 | 14–46 | 3.8 |
| -10 | 18.59 | 27.77 | 17.04 | 5–41 | 4.9 |
| -11 | 18.59 | 7.04 | 4.26 | 4–27 | 5.0 |
| -12 | 1.86 | 0.013 | 8.71 | 18–62 | 3.7 |
| -13 | 0.93 | .0066 | 8.71 | 20–60 | 3.9 |
| | | | | | Av. 4.9 ± 0.6 |
| 3-1 | 9.30 | .066 | 21.8 | 33–63 | 7.1 |
| -2[e] | 4.65 | .033 | 21.8 | 30–62 | 4.6 |
| -3[e] | 1.86 | .013 | 8.71 | 22–65 | 6.6 |
| -4 | 0.93 | .0066 | 8.71 | 14–63 | 4.4 |
| -5[d] | 0.465 | .0033 | 4.35 | 20–64 | 6.4 |
| | | | | | Av. 5.8 ± 1 |
| 4-1 | 4.65 | .033 | 8.71 | 30–75 | 15.1 |
| -2 | 2.79 | .020 | 2.18 | 17–60 | 15.2 |
| -3[d] | 0.93 | .0066 | 4.35 | 16–67 | 9.9 |
| | | | | | Av. 13.4 ± 2.3 |
| 5-1 | 12.37 | 7.00 | 8.71 | 36–83 | 60 |
| -2 | 4.65 | 0.033 | 4.35 | 31–66 | 38 |
| -3 | 2.79 | .020 | 2.18 | 26–69 | 48 |
| -4[d] | 0.93 | .0066 | 4.35 | 30–76 | 30 |
| -5[d] | 0.465 | .0033 | 4.35 | 29–80 | 22 |
| | | | | | Av. 40 ± 11 |

[a] The initial number designates the reaction medium. [b] Measurements made at 500 mμ only unless otherwise noted. [c] The listed uncertainty is the average difference between the average value and the individual values. The temperature uncertainty contributes an uncertainty of ±6% to the value of $k$. [d] Measurements made at 492 mμ. [e] Measurements made at both wave lengths.

in the reduction of chromium(VI) by iron(II).[4,5a] Perhaps it is only at this step that a change in coördination number of chromium occurs.[1] The problem is not, however, as stated by Waters,[5c] ". . . . to know when, and how, this removal of oxygen (from $CrO_4^=$ to give $Cr^{+++}$) occurs," but rather to know the stage at which, in the reduction of chromium(VI), the coördination number increases; one cannot argue against the existence of $Cr(OH_2)_6^{+3}$ as the form of chromium(III) in the acidic non-complexing media. Chromium(IV), like chromium(III), may have coördination number 6, and chromium(V), like chromium(VI), may have coördination number 4. The latter possibility is quite reasonable since manganese(VI), which is isoelectronic with chromium(V), has coördination number 4, and direct experimental evidence supporting a tetrahedral configuration for hypochromate ion $CrO_4^≡$ has been obtained by Bailey and Symons.[17] It is also relevant that the X-ray diffraction pattern of $Ba_3(CrO_4)_2$ is very similar to that shown by $Ba_3(PO_4)_2$.[18] There is also some experimental evidence supporting the suggestion that the coördination number of chromium(IV) is six. The similarity of the visible spectra of ammonium vanadium alum, containing hexaaquovanadium(III) ion, and vanadium(III) ion in solution[19] indicates coördination number six for the latter species, which is isoelectronic with chromium(IV). The compounds $K_2CrF_6$ and $K_2MnF_6$ have the same X-ray diffraction pattern; in the latter compound, manganese(IV) has six fluoride ions around it in an octahedral arrangement.[20]

(17) N. Bailey and M. C. R. Symons, *J. Chem. Soc.*, 203 (1957).

(18) J. Kleinberg, *J. Chem. Ed.*, **33**, 73 (1956).

(19) O. G. Holmes and D. S. McClure. *J. Chem. Phys.*, **26**, 1686 (1957).

(20) E. Huss and W. Klemm, *Z. anorg. Chem.*, **262**, 25 (1950); W. Klemm, *Angew. Chem.*, **66**, 468 (1954).

The inverse dependence of the cerium(IV)-chromium(III) reaction rate upon the concentration of bisulfate ion or upon both the concentration of hydrogen ion and sulfate ion is reasonable. The final products of the reaction are both less cationic and probably less complexed by sulfate ion than are the reactants. As is generally the case under such circumstances, it is energetically profitable for some of the positive charge and sulfate ions to be lost prior to the formation of the transition-state.[21]

[21] E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY, JERUSALEM, ISRAEL]

# The Influence of Ionic Strength and of Temperature on the Rate of Oxidation of D-Glucose by Bromine

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The influence of ionic strength on the rate of oxidation of D-glucose by bromine in aqueous solution has been shown to support the previous assumption that in strongly acid solution molecular bromine reacts with the D-glucose *molecule*, whereas in moderately acid solution, it reacts with the *anion* of D-glucose. The energies of activation for the two reactions have been determined. The high value of the rate constant for the reaction between bromine and the D-glucose anion has been shown to be due to a low energy of activation, the $P_Z$-factors being practically identical.

We have shown recently[1] that the oxidation of D-glucose in bromine water proceeds *via* molecular bromine and that the $p$H dependence of the rate of reaction is consistent with the assumption that the anionic form of D-glucose is oxidized much faster than D-glucose itself. We thought it desirable to substantiate this assumption by further experiments and therefore investigated the influence of ionic strength in somewhat greater detail and also measured the influence of temperature on the reaction rate.

## Methods

**The experimental procedure** was the same as in our previous work.[1]

**The influence of the ionic strength** was investigated in solutions containing a mixture of bromine and hypobromous acid. As described in section 4 of our previous paper,[1] this enables the reaction to be carried out at very low buffer concentration and therefore at low ionic strength. We again[1] achieved the $p$H by the addition of sulfuric acid and chose the values of $p$H of 1.5 and 3.03 (at an acid concentration corresponding to a $p$H markedly higher than 3.03, the buffer-capacity of the acid would become insufficient). The rate equation has been shown[1] to be

$$\frac{dx}{dt} = k_{Br_2}\left[(c + x) + \frac{k_{HOBr}}{k_{Br_2}}(e - 2x)\right][\beta\text{-D-glucose}] \quad (1)$$

where $c$ and $e$ are the initial concentrations of bromine and of hypobromous acid, respectively, and $x$ the concentration of the product formed at time $t$. At $p$H 3.03, the second member in the square brackets is negligible; at $p$H 1.5 it is small, and no appreciable error is introduced if we assume $k_{HOBr}/k_{Br_2}$ to be independent of the ionic strength.

The ionic strength was varied by adding the uni-univalent electrolyte sodium nitrate.

**The influence of temperature** was investigated in solutions containing bromine to which bromide at an initial concentration of 0.187 $M$ had been added. Because of the tribromide formed in this mixture (*cf.* section 2 of our previous paper[1]) the reaction is slowed down sufficiently for kinetic measurements at temperatures above 0° to be carried out conveniently. The rate constant was calculated from

$$\frac{dx}{dt} = k_{Br_2}\frac{K_3}{K_3 + [Br^-]}(a - x)[\beta\text{-D-glucose}] \quad (2)$$

where $K_3$ is the dissociation constant of tribromide (*cf.* equations 1 and 6 of our previous paper[1]).

The values of $p$H were 1.57 which again[1] was achieved by the addition of sulfuric acid, and 4.04 and 4.55 at which acetate buffers were employed.

The temperatures used were 0 and 25° at $p$H 1.57 and 0, 9.4 and 25° at the other two values of $p$H. The temperature control was ± 0.08° or better.

The values of $K_3$ employed at 0 and 25° were 0.051 and 0.0625, as measured by Jones, *et al.*[2,3] At 9.4°, we assumed $K_3$ to be equal to 0.053. This was obtained from an interpolation of the log $K_3$ *vs.* $1/T$ plot (Fig. 1, crosses), in which we inserted also the values of Griffith, McKeown and Winn[4] at 16.5 and 21.5°. As can be seen from the figure, the various values are not entirely consistent with each other. However, the error introduced into $k_{Br_2}$ by a possible error in $K_3$ is not too serious, since (a) the temperature dependence of $K_3$ is only slight in comparison with that of the experimental rate constant and (b) expression 2 is less sensitive to changes in $K_3$ than would be an expression directly proportional to $K_3$.

## Results and Discussion

1. **Influence of Ionic Strength.**—At $p$H 3.03, a pronounced positive salt-effect was observed. This is illustrated by Fig. 2, where log $k_{Br_2}$ has been plotted against the square root of the ionic strength (circles). On the basis of the assumption that at this $p$H the reaction takes place between bromine and the glucose anion, this can be interpreted as a typical secondary salt-effect, affecting the degree of dissociation of glucose. At constant $p$H, the slope in Fig. 2 should be 0.5 provided the Debye Limiting Law is applicable. Our experimental value is about 0.4 at the lowest concentration amenable to measurement; the difference may well be due to a failure of the Limiting Law at these concentrations. The slope of course decreases further with increasing ionic strength.

On the other hand, at $p$H 1.5 the increase of the rate-constant remained within the limit of experimental error when the ionic strength was changed from 0.03 to 0.28 (see Fig. 2, crosses). This is entirely consistent with the assumption of a reaction between two molecules, *viz.*, glucose and bromine.

2. **Influence of Temperature.**—In Fig. 1, log $k_{Br_2}$ has been plotted *vs.* $(1/T)$. The lines for $p$H 4.04 and 4.55 are seen to be parallel (half-closed

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[1] B. Perlmutter-Hayman and A. Persky, THIS JOURNAL, **82**, 276 (1960).

[2] Grinnell Jones and M. L. Hartman, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

[3] Grinnell Jones and S. Baeckström, THIS JOURNAL, **56**, 1517 (1934).

[4] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932).