

A Kinetic Study of the Reaction between Chromium(VI) and Hydroquinone¹

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For the reaction $2\text{Cr(VI)} + 3(\text{hydroquinone}) = 2\text{Cr(III)} + 3(\text{quinone})$, the empirical form of the rate law in a perchloric acid–lithium perchlorate media is $-d\text{Cr(VI)}/dt = k'[\text{Cr(VI)}][\text{hydroquinone}][\text{H}^+]^{1.25}$. The variation of k' with temperature and ionic strength changes are presented. No spectrophotometric evidence was obtained for the presence of an intermediate.

Introduction

When hydroquinone is oxidized by the one-equivalent acceptor Fe(III), the empirical form of the rate law suggests that the semiquinone radical is of kinetic importance.³ If the 2-equiv. acceptor NaIO₄ is used as the oxidant, the results are interpreted in terms of second-order kinetics.⁴ In the present investigation the 3-equiv. acceptor Cr(VI) has been used as the oxidant. In a multi-equivalent reaction⁵ the empirical form of the rate law may provide evidence consistent with the interpretation that intermediate oxidation states are of kinetic significance.

Experimental Section

The preparation and standardization of the perchloric acid, lithium perchlorate, and Cr(VI) stock solutions have been described in a previous publication.⁶ The benzoquinone was purified by sublimation. The hydroquinone was purified by vacuum sublimation (m.p. 172.8–173.2°). An alternate method, recrystallization from dilute acid, was used to obtain a second stock source of the hydroquinone.

The reactions were carried out in 2-, 5-, or 10-cm. cylindrical silica absorption cells. The cell compartment of the Cary Model 14 spectrophotometer used was thermostated to $\pm 0.1^\circ$ of the working temperature.

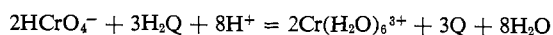
Weighed amounts of Cr(VI) solutions containing the appropriate concentrations of perchloric acid, lithium perchlorate, and, when applicable, benzoquinone or Cr(III) perchlorate were added to the cells at room temperature. After temperature equilibrium was attained, an aliquot of the hydroquinone (from a stock solution maintained at the working temperature) was rapidly injected into the cell. The change in optical density at 3500 Å. was recorded as a function of elapsed time. Concentrations were calculated for from 10 to 30

different values of the recorded optical density in each kinetic experiment. In these experiments the initial concentrations of the reactants were ca. $5\text{--}20 \times 10^{-5} M$.

Two sets of kinetic experiments were carried out using a stopped-flow apparatus⁷ similar to that described by Dulz and Sutin.⁸

Results and Discussion

For the reaction



the stoichiometry and product identity were established by the following procedures. A weighed amount of a Cr(VI) solution ($7.02 \times 10^{-4} M$) was added to a measured volume of a $2.00 \times 10^{-3} M$ solution of hydroquinone in $10^{-2} M$ perchloric acid. The ratio of Cr(VI) consumed to hydroquinone consumed was 0.652 ± 0.013 . Cr(VI) concentrations were determined spectrophotometrically at 3500 Å. where the pertinent molar absorptivities ($\text{l. mole}^{-1} \text{ cm.}^{-1}$) were 1584 ± 14 and 20 ± 1 for the Cr(VI) and quinone, respectively. Hydroquinone is essentially transparent at this wave length.

The Cr(III) species produced in a reaction mixture of the same concentrations was characterized by ion-exchange separation⁹ and spectrophotometric observation of the hexaaquochromium(III) absorption bands. Benzoquinone was identified spectrophotometrically after extraction into CCl₄ from a similar reaction mixture.

Kinetic Results. The reaction was first order in both Cr(VI) and hydroquinone under all our experimental conditions.¹⁰ The apparent rate constant k' is defined by

$$-d[\text{Cr(VI)}]/dt = k'[\text{Cr(VI)}][\text{H}_2\text{Q}] \quad (1)$$

where H₂Q is the concentration of hydroquinone. The usual integrated form of eq. 1 was used to calculate the values of k' ¹¹ which will be presented.

Table I summarizes the values obtained for k' at 25°, $\mu = 5.00 \times 10^{-2}$ at an acidity of $1.00 \times 10^{-2} M$

(7) These experiments were carried out at the University of Chicago through the courtesy of Professor J. Halpern who made available the stopped-flow apparatus.

(8) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(9) J. L. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(10) In experiments where the solutions were deoxygenated using purified nitrogen, the results were identical with those obtained when this procedure was omitted. Therefore, the data presented are for solutions containing the normal amount of dissolved oxygen.

(11) Values of k' were calculated by a weighted least-squares adjustment of the data for the indefinite integral of (1). Initial estimates of the weights were obtained by assuming an uncertainty of ± 0.002 in the measured optical densities. The computer facilities of the Applied Mathematics Division were used for these calculations.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Temporary summer employee.

(3) J. H. Baxendale, H. R. Hardy, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **47**, 963 (1951).

(4) E. T. Kaiser and S. W. Weidman, *J. Am. Chem. Soc.*, **86**, 4354 (1964).

(5) This description of the system as a "multi-equivalent reaction," corresponds to the classification suggested by J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

(6) J. C. Sullivan, *J. Am. Chem. Soc.*, **87**, 1495 (1965).

perchloric acid. These data substantiate the statement made previously that the reaction is first order in both of the reactants. In addition there is, not unexpectedly, no effect of the products on the rate of the reaction.

Table I.^a Values of k' at 25°, $[H^+] = 1.00 \times 10^{-2} M$, $\mu = 5.00 \times 10^{-2}$ (LiClO₄)

[Cr(VI)] ₀ × 10 ⁵ moles/l.	[Hydroquinone] ₀ × 10 ⁴ moles/l.	k' , l. mole ⁻¹ sec. ⁻¹
8.69	1.64	55.5 ± 1.5
8.43	1.82	54.1 ± 0.9 ^b
8.72	2.32	52.1 ± 0.1
9.55	1.47	53.1 ± 0.1 ^c
9.80	1.47	53.1 ± 2.7
9.80	1.47	53.2 ± 0.2 ^d
10.55	0.695	55.0 ± 0.7
17.5	2.32	52.1 ± 0.1
17.6	1.65	52.4 ± 0.3
		$\langle k' \rangle = 53.4 \pm 1.2$

^a Uncertainties are the standard deviations from replicate experiments. ^b Hydroquinone and Na₂Cr₂O₇ recrystallized from distilled water. Other entries used sublimed hydroquinone and N.B.S. K₂Cr₂O₇. ^c Initial Cr(III) concentration $1.05 \times 10^{-4} M$. ^d Initial benzoquinone concentration $1.50 \times 10^{-4} M$.

The least-squares values determined for n (when eq. 2 is transformed into the usual logarithmic form) are 1.24 ± 0.03 , 1.30 ± 0.02 , and 1.25 ± 0.01 at 25, 15, and 5°, respectively.

An alternative method of describing the variation of k' with change in hydrogen ion concentration is the usual power series development, *i.e.*¹²

$$k' = a + b[H^+] + c[H^+]^2 \quad (3)$$

The values that were obtained for a are: $-3.4 \times 10^{-4} \pm 2.8 \times 10^{-2}$, $-8.0 \times 10^{-4} \pm 2.9 \times 10^{-2}$, and $-9.1 \times 10^{-4} \pm 1.9 \times 10^{-2}$; for b : $(4.56 \pm 0.38) \times 10^3$, $(3.13 \pm 0.12) \times 10^3$, and $(2.62 \pm 0.08) \times 10^3$; for c : $(9.4 \pm 2.4) \times 10^4$, $(7.66 \pm 0.74) \times 10^4$, and $(5.03 \pm 0.42) \times 10^4$ at 25, 15, and 5°, respectively.

The parameters b and c are identified as rate coefficients for parallel reaction paths with activated complexes containing one and two hydrogen ions, respectively, in addition to the molecules of hydroquinone and HCrO₄⁻. The latter are the predominant species at the acid and reactant concentrations used.

The proposed mechanism of hydrogen ion catalysis is not unique. One source of ambiguity arises from the fact that a power series adjustment of the data was used.

Table II. $[H^+]$ and Temperature Dependency of k' ^a

5°		15°		25°	
[H ⁺] × 10 ² , moles/l.	k' , l. mole ⁻¹ sec. ⁻¹	[H ⁺] × 10 ² , moles/l.	k' , l. mole ⁻¹ sec. ⁻¹	[H ⁺] × 10 ² , moles/l.	k' , l. mole ⁻¹ sec. ⁻¹
0.399	10.4 ± 0.2	0.399	12.5 ± 0.2	0.410	18.5 ± 0.1
0.596	18.1 ± 0.1	0.596	22.6 ± 0.5	1.00	53.4 ± 1.2
0.795	24.2 ± 0.1	0.800	31.8 ± 0.1	1.50	95.2 ± 1.3
0.998	32.8 ± 0.1	1.00	41.7 ± 2.6	2.00	140.4 ± 0.9
2.98	128.4 ± 0.5	3.00	179.9 ± 1.7	4.00	299.8 ± 2.0
4.99	245.2 ± 4.2	5.00	332.5 ± 13.1		

^a $\mu = 5.00 \times 10^{-2}$, $[Cr(VI)]_0 = 6.2 \times 10^{-4} - 6 \times 10^{-6} M$, $[hydroquinone]_0 = 1.3 \times 10^{-4} - 6.0 \times 10^{-6} M$. All values are the average of from two to four independent determinations.

Table III. Effect of Changing Ionic Strength^a at 25°

μ	k' , l. mole ⁻¹ sec. ⁻¹
1.0×10^{-2}	63.8 ± 1.6
5.0×10^{-2}	53.5 ± 1.8
0.246	40.9 ± 0.4
0.560	40.0 ± 0.2
1.00	43.1 ± 2.6
1.58	52.5 ± 0.4
2.00	57.4 ± 0.2

^a $1.00 \times 10^{-2} M HClO_4$, $[Cr(VI)]_0 = 1.50 \times 10^{-4} M$, $[hydroquinone]_0 = 1.70 \times 10^{-4} M$, μ maintained with LiClO₄.

Effects of $[H^+]$. Temperature and LiClO₄. Table II summarizes the data obtained when the hydrogen ion concentration and the temperature are varied.

In Table III data are presented which indicate the variation to be observed in the rate parameter k' when the ionic strength is varied.

The empirical form of the rate expression which summarizes the variation in k' with change in hydrogen ion concentration is

$$k' = k''[H^+]^n \quad (2)$$

The coefficients of such a series can be considered as describing multiple parallel paths or a single path plus correction terms for the variation of activity coefficient ratios with change in solution composition.¹³

The magnitude of the change in k' with increasing LiClO₄ concentration, at constant hydrogen ion concentration, is a point for the interpretation we have advanced. The maximum change in k' (see Table III) is *ca.* 63% for a 56-fold change of lithium perchlorate concentration. On the assumption of a single path plus activity coefficient changes, $k'/[H^+]$ varies by a factor of two for a tenfold change of perchloric acid concentration at constant ionic strength.

The energies of activation calculated from the temperature variation of the rate parameters b and c are 4.6 ± 1.0 and 5.2 ± 0.9 kcal./mole. It is of interest to recall that these values are of the same order of magnitude as the energy of activation for diffusion in solution. However, since the empirical formula of the activated complexes indicates the presence of three and

(12) If a simple and chemically satisfying interpretation of the data is possible, the statistical adjustment in terms of eq. 3 can be expected to produce values of a which will be spanned by one standard deviation.

(13) For a thorough analysis of this problem, see T. W. Newton and F. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

four molecules (in addition to an unknown number of solvent molecules), this information does not assist in the development of a detailed reaction mechanism.

Mechanistic Considerations. By analogy with the extensive work of Westheimer and his collaborators¹⁴ on the chromic acid oxidation of alcohols, one plausible mechanism for the present reaction would involve the formation of a chromium ester. Attempts to prepare the chromic acid ester of hydroquinone¹⁵ failed to provide conclusive evidence¹⁶ for the existence of such a species.

An additional effort was made to demonstrate the possible existence of the ester by carrying out experiments at markedly higher concentrations of hydroquinone using a stopped-flow system.¹⁷

(14) See, for example, Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 1401 (1960), and the references therein cited.

(15) The techniques were essentially those described by F. Holloway, M. Cohen, and F. H. Westheimer, *ibid.*, **73**, 65 (1951).

(16) Spectrophotometric observations on the yellow benzene layer were ambiguous. Attempts to determine the presence of chromium in this layer after evaporation did not succeed.

(17) These experiments were carried out under the guidance of Dr. R. Palmer. The solutions of perchloric acid and chromium(VI) were

Kinetic experiments were carried out at 25°, $[\text{Cr(VI)}]_0 = 2.5 \times 10^{-4} M$ and hydroquinone = 1.55 and $4.72 \times 10^{-2} M$. No evidence was found to indicate the existence of an intermediate. Pseudo-first-order kinetics were observed in all 14 independent experiments. At an initial hydroquinone concentration of $1.55 \times 10^{-2} M$, the average value (five determinations) calculated for k was $5.65 \pm 0.13 \text{ sec.}^{-1}$, and at $4.72 \times 10^{-2} M$ hydroquinone the average value (eight determinations) was $k = 18.1 \pm 1.0 \text{ sec.}^{-1}$.

These values when converted to second-order rate constants ($\text{l. mole}^{-1} \text{ sec.}^{-1}$) are 365 ± 8 and 383 ± 21 , respectively. From the empirical form of the rate law previously determined,¹⁸ the value calculated at a hydrogen ion concentration of $0.0472 M$ is $k' = 383 \pm 15$. While these results provide an excellent check on the value of the empirical rate constant, they cannot provide the basis for any detailed insight into the mechanism of the reaction.

provided by Dr. Palmer. The distilled water at Kent Laboratory was used in the preparation of the hydroquinone solutions.

(18) $\text{Log } k' = 4.227 \pm 0.058 + (1.239 \pm 0.031) \text{ log } [\text{H}^+]$, determined from the data in Table II.