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# A Spectrophotometric Study of the Rate of Formation of Violet Peroxychromate in Aqueous Solution

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A Spectrophotometric Study of  
the Rate of Formation of Violet Peroxychromate in Aqueous  
Solution

by

Pref. David M. Hayes and Stephan N. Witt  
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### Abstract

HAYES, DAVID M., and WITT, STEPHAN M. A Spectrophotometric Study of the Rate of Formation of Violet Perchromate in Aqueous Solution. Department of Chemistry, June 1961.

The rate of formation of violet peroxochromate ( $\text{HCrO}_6^-$ ) in aqueous solution was monitored spectrophotometrically at 540 m $\mu$ . The method of initial rates enabled us to determine the exponents, x, y, and z, in the rate law for the violet species.

**Rate Law.**  $d[\text{violet}]/dt = k[\text{HCrO}_4^-]^x [\text{H}^+]^y [\text{H}_2\text{O}_2]^z$ .

The reaction was determined to be third order overall, being first order in  $\text{HCrO}_4^-$ ,  $\text{H}^+$ , and  $\text{H}_2\text{O}_2$ . The rate constant for violet's formation is,

$$k_{\text{violet}} = 10^{7.9} \exp(-5100 \text{ cal/RT}) .$$

Comparison of the kinetics of formation of the violet species, in slightly acidic solution, to the kinetics of formation of  $\text{CrO}_5 \cdot \text{H}_2\text{O}$ , in strongly acid solution, reveals that both species most likely form by the same mechanism. The pH of the solution governs whether  $\text{CrO}_5 \cdot \text{H}_2\text{O}$  or  $\text{HCrO}_6^-$  will form.

Acknowledgment

We would like to thank Professor Scalfi and Professor Weisk for many fruitful discussions throughout the year. Also, thanks to GE Sillicone for the use of the thermocouples, the calibrated Transicator 430 A., and the Digital Display Unit (Newport Laboratories).

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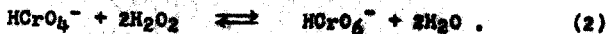
A Spectrophotometric Study of the Rate  
of Formation of Violet Peroxychromate in Aqueous Solution

**Introduction.** When hydrogen peroxide is added to a strongly acidic solution of dichromate the well known blue peroxychromic acid ( $\text{CrO}_5 \cdot \text{H}_2\text{O}$ ) forms,



The kinetics of formation of blue peroxychromic acid have been studied by Moore, Kettle, and Wilkins<sup>1</sup> and Orhanovic and Wilkins<sup>2</sup>. The reaction is third order overall, being first order in  $\text{H}^+$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HCrO}_4^-$ . The rate constant at 25°C and an ionic strength of 0.1 M is  $2.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$ .

When hydrogen peroxide is added to a dichromate solution with a pH of from 4.0 to 7.0  $\text{HCrO}_6^-$  forms.



$\text{HCrO}_6^-$  is the conjugate base of blue peroxychromic acid. Both species decompose rapidly in aqueous solution. The composition of violet peroxychromate has been determined from chemical and spectral data by Griffith<sup>3</sup>.  $\text{CrO}_5 \cdot \text{H}_2\text{O}$  and  $\text{HCrO}_6^-$  both have two peroxy groups attached to the central chromium (VI) atom forming two three-membered rings with a common corner. The water of hydration in the blue species is replaced by  $\text{OH}^-$  in the violet species; the violet species is more aptly written as  $\text{CrO}_5(\text{OH})^-$ .

$\text{CrO}_5(\text{OH})^-$  is an intermediate in the decomposition of hydrogen peroxide. The decomposition of  $\text{H}_2\text{O}_2$  by chromium (VI) salts has been studied by Spitalsky<sup>4</sup> and by Kebesev<sup>5</sup>. The decomposition of  $\text{H}_2\text{O}_2$  by dichromate

solutions has been likened to the decomposition of  $H_2O_2$  by iron-salts<sup>6</sup>. Various cyclic oxidation-reduction mechanisms involving the chromium atom in  $HCrO_6^-$  have been postulated to account for the decomposition of  $H_2O_2$ <sup>4,5</sup>.

This study has been concerned with the formation reaction of violet peroxychromate. The formation of the violet species is sufficiently rapid to warrant study by stopped-flow techniques, ( $t_{1/2} \approx 2$  sec.). It is of particular interest to compare the kinetics of formation of the violet species to the kinetics of formation of the blue species since their structures are so similar.

The exponents in the rate law of the violet species,

$$d[\text{violet}]/dt = k [HCrO_4^-]^x [H^+]^y [H_2O_2]^z \quad (3)$$

were determined by the method of initial rates. The progress of the reaction with time was followed by monitoring the formation of  $HCrO_6^-$  spectrophotometrically at 540 nm. The concentration of  $HCrO_6^-$  was calculated from the measured absorbance using an extinction coefficient from Bartlett and Quane<sup>7</sup> ( $\epsilon_{540} = 510 \text{ M}^{-1}\text{cm}^{-1}$ ).

The rate of reaction (2) was studied at three temperatures, 15°C, 25°C, and 35°C. In each case, plots of  $HCrO_6^-$  vs. time were made. The initial slopes of these curves are equal to the initial rate of each reaction. By comparing the effect of systematic variations of initial reactant concentrations on the initial rates, it is possible to determine the correct exponents,

x, y, and z, in the rate expression. The rate constant is then calculated using equation (4).

$$k = (d[\text{HCrO}_4^-]/dt)/([\text{HCrO}_4^-]^x [\text{H}^+]^y [\text{H}_2\text{O}_2]^z) . \quad (4)$$

### Experimental Section

Materials. All of the reagents used were reagent grade without any further purification. Deionized water was used in all of the solutions. A weighed sample of  $\text{K}_2\text{Cr}_2\text{O}_7$  (Matheson, Coleman, and Bell) was dissolved in a volumetric flask to give a stock solution of  $5.41 \times 10^{-3}$  M. Solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  that are approximately  $10^{-3}$  M are 90-95 % in the form of  $\text{HCrO}_4^-$ . The hydrogen peroxide stock solution (1.63M), was prepared with 30% hydrogen peroxide from the Fisher Scientific Co. The hydrogen peroxide stock solution was standardized daily with a standard solution of  $\text{KMnO}_4$ . The  $\text{KMnO}_4$  was purchased from the Fisher Scientific Co. The potassium permanganate solution was standardized with a primary standard, sodium oxalate, purchased from the Fisher Scientific Co. A weighed sample of  $\text{KNO}_3$  (Fisher Scientific Co.) was dissolved to give a stock solution of 0.87 M. The potassium nitrate stock solution was used to adjust the ionic strength of the solutions used in the kinetic runs to 0.1 M.

### Preparation of the solutions for the kinetic runs.

Each kinetic run consisted of two solutions that are prepared separately, then mixed in the mixing chamber of a stopped-flow apparatus. The acidic dichro-

mate solutions contained predominantly  $\text{HCrO}_4^-$ ,  $\text{H}^+$ , and  $\text{KNO}_3$ , while the acidic hydrogen peroxide solutions contained  $\text{H}_2\text{O}_2$ ,  $\text{H}^+$ , and  $\text{KNO}_3$ . Four kinetic runs were done at each temperature. The first run, the reference run, typically had upon mixing  $[\text{HCrO}_4^-] = 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 0.60 \text{ M}$  and a pH of approximately 4.1. (See Table I) The concentrations of  $\text{HCrO}_4^-$ ,  $\text{H}^+$ , and  $\text{H}_2\text{O}_2$  were varied independently in the three remaining runs at each temperature.

The preparation of the acidic  $\text{HCrO}_4^-$  and the acidic hydrogen peroxide solutions were carried out as follows. Forty-five milliliters of the potassium dichromate stock solution were diluted to 200 mls. in a volumetric flask. Enough  $\text{KNO}_3$  was added to yield a solution of ionic strength equal to 0.1 M. For the acidic hydrogen peroxide solutions, typically from 150-170 mls. of the hydrogen peroxide stock solution was diluted in a 200 ml. volumetric flask. Once again, the quantity of  $\text{KNO}_3$  added was such as to yield a solution of 0.1 M ionic strength. Each solution was then placed in a constant temperature bath that maintained the temperature to  $\pm 0.1^\circ\text{C}$ . (Neslab Refrigerated Bath, Model RTE-9.)

Next, the pH of each solution was measured with an Orion Research Model 701 A/digital pH meter. The pH meter was calibrated using a Fisher pre-mixed buffer ( $\text{pH} = 4.01 \pm .02$  at  $25^\circ\text{C}$ ), that was also placed in the constant temperature bath. After calibration of the pH meter



Table I  
Solution Preparation for the Kinetic Runs

Temp. (°C) ± 0.2	Run	HCrO <sub>4</sub> <sup>-</sup> (M)	pH	H <sub>2</sub> O <sub>2</sub> (M)
15	1	1.09 x 10 <sup>-3</sup>	4.06	0.701
	2	5.13 x 10 <sup>-4</sup>	4.06	0.701
	3	1.09 x 10 <sup>-3</sup>	4.07	0.289
	4	1.09 x 10 <sup>-3</sup>	4.50	0.701
25	1	1.06 x 10 <sup>-3</sup>	4.03	0.611
	2	4.91 x 10 <sup>-4</sup>	4.04	0.611
	3	1.06 x 10 <sup>-3</sup>	4.03	0.204
	4	1.06 x 10 <sup>-3</sup>	4.51	0.611
35	1	1.08 x 10 <sup>-3</sup>	4.08	0.608
	2	4.95 x 10 <sup>-4</sup>	4.08	0.608
	3	1.08 x 10 <sup>-3</sup>	4.08	0.197
	4	1.08 x 10 <sup>-3</sup>	4.51	0.608

at the temperature of the solutions, the pH was measured. Initial values for the pH of the  $\text{HCrO}_4^-$  solutions fell in the range from 4.4 - 4.7; whereas, initial measurements of the pH of the hydrogen peroxide solutions fell in the range from 4.6 - 4.9. The pH of each solution in a kinetic run had to be virtually identical, since a small difference, ( $\pm .03$ ), in the pH's of the two solutions in a run could result in as much as a 7% difference in the hydrogen ion concentration of the two solutions. A method was developed whereby the pH of the solutions were manipulated without significantly altering the initial volume of 200 mls.

Adjusting the pH of the acidic  $\text{HCrO}_4^-$  and the acidic hydrogen peroxide solutions to a pH of approximately 4.0 without a significant change in the total volume of 200 mls. was accomplished by micropipetting either a solution of KOH or  $\text{HNO}_3$  into the kinetic solutions. The potassium hydroxide was Laboratory Grade from Fisher Scientific Co. The nitric acid was from J.T. Baker Co. In the process of manipulating the pH of each solution, never more than 0.5 mls. of acid or base solution were added, therefore, neither the concentrations of  $\text{H}_2\text{O}_2$  or  $\text{HCrO}_4^-$  were significantly affected. Nor was the ionic strength altered significantly due to the addition of the minute amount of ions added to change the pH from about 4.5 to 4.1.

Kinetic Runs. After preparing the acidic  $\text{HCrO}_4^-$  and the acidic hydrogen peroxide solutions, both solutions were

injected into separate polyethylene holding syringes within the Aminco-Morrow Stopped-Flow Apparatus (American Instruments Co., Inc.). The holding syringes were bathed in water that flowed from the constant temperature bath used for the equilibration of the solutions while measuring the pH. Each polyethylene syringe had a hole drilled into the wall of the cell within two mm. of the interior of the syringe - a thermocouple was inserted into each hole. Using the thermocouples, the temperature of the interior of the syringe was monitored directly rather than relying on the temperature measured by a thermometer positioned in the constant temperature bath itself. Independent tests indicated that the temperatures within the wall of the polyethylene syringes measured by the thermocouples agreed to the temperatures of the solutions inside the syringes to within  $0.2^{\circ}\text{C}$ . The temperatures measured by the thermocouples were displayed on a calibrated Trendicator 410 A, Digital Display Unit, Model 810, from Newport Laboratories.

For the kinetic runs at  $15^{\circ}\text{C}$  a flow of dry nitrogen was directed around the mixing chamber to prevent fogging of the windows of the chamber.

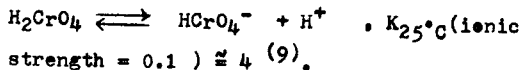
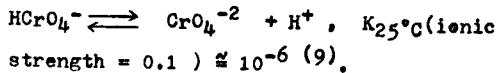
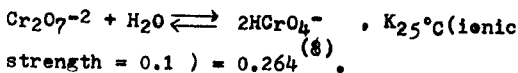
Apparatus. The reaction was monitored spectrophotometrically by following formation of the violet peroxychromate at 540 nm. (Beckman D.U., National Technical Laboratories). The output was displayed on a Tektronix storage oscilloscope, Model T912.

### Results

We determined the rate law for the formation of violet peroxychromate at 15 °C, 25 °C, and 35 °C. In each case, an expression of the form

$$d[\text{HCrO}_4^-]/dt = k[\text{HCrO}_4^-]^x [\text{H}^+]^y [\text{H}_2\text{O}_2]^z$$

fit the data well. The exponents found for each temperature are presented in Table II and appear to be the same for all temperatures. Given the uncertainties in the measurement of each exponent, we think it reasonable to conclude that each exponent is unity at all temperatures studied. There are three equilibria involving chromium which potentially could affect the determination of x.



Under the conditions of this experiment ( pH  $\cong$  4,  $\text{K}_2\text{Cr}_2\text{O}_7 \cong 5 \times 10^{-4}$  M ), both  $\text{CrO}_4^{-2}$  and  $\text{H}_2\text{CrO}_4$  represent less than 1 % of the total chromium in solution. Approximately 5 % of the chromium, however, is present as dichromate with the balance, ~~95~~ 95 %, as  $\text{HCrO}_4^-$ . The quantity  $\text{HCrO}_4^-$  which appears in the rate law represents actual  $\text{HCrO}_4^-$  concentration, not the sum of  $\text{Cr}_2\text{O}_7^{-2}$  and  $\text{HCrO}_4^-$ . The equilibrium constants for  $\text{Cr}_2\text{O}_7^{-2} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$  at 15 °C, 25 °C, and 35 °C are, respectively, 0.0188 M, 0.0264 M, and 0.0340 M.

They were estimated for these three temperatures and an ionic strength of 0.1 using values measured by Teng and King<sup>8</sup> and Davies and Prue<sup>10</sup>.

We have calculated the observed rate constants at the three temperatures studied and present the results in Table III. The rate constants are calculated directly from the measured initial rates and initial concentrations using exponents of exactly one for each species appearing in the rate expression. The extinction coefficient for  $\text{HCrO}_6^-$ ,  $\epsilon_{540} = 510 \text{ M}^{-1}\text{cm}^{-1}$ , was taken from the work of Bartlett and Quane<sup>7</sup>. A plot of  $\ln k$  versus  $1/T$ , Figure 1, gives an Arrhenius activation energy for the reaction of 5100 calories. The Arrhenius pre-exponential factor is  $10^{7.9}$ .

Table II

Rate Law Exponents

<u>Temp. (C) <math>\pm 0.2</math></u>	<u>x</u>	<u>y</u>	<u>z</u>
15	1.05	0.97	0.98
25	1.15	0.88	1.00
35	0.88	0.94	0.92

Table III

Rate Constants

<u>Temp. (C) <math>\pm 0.2</math></u>	<u>k (M<sup>-2</sup>s<sup>-1</sup>)</u>
15	$1.02 \times 10^4$
25	$1.54 \times 10^4$
35	$1.83 \times 10^4$

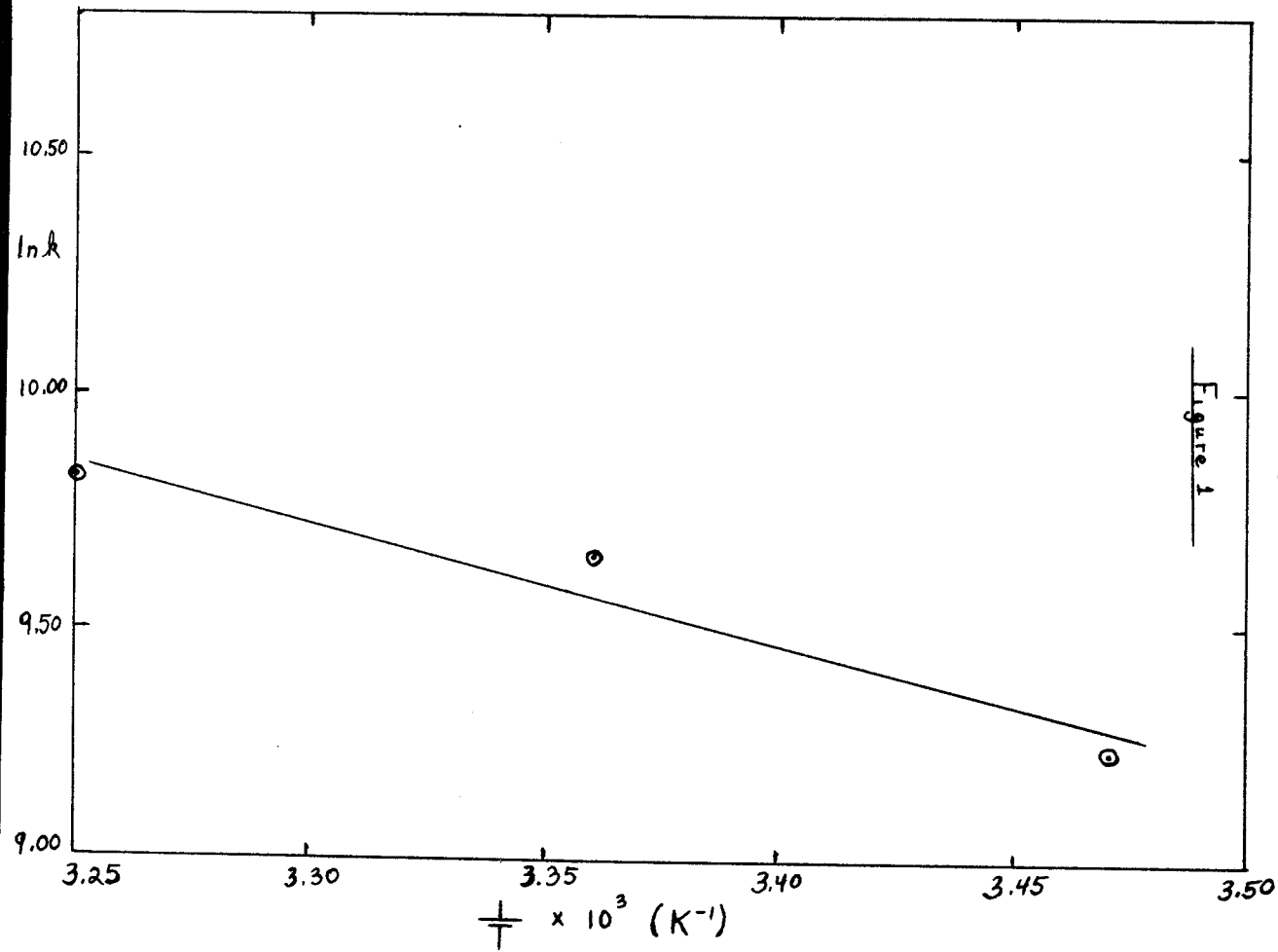


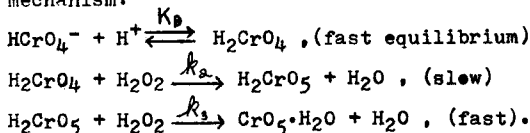
Figure 1

Discussion

Moore, Kettle, and Wilkins<sup>1</sup> and Orhanovic and Wilkins<sup>2</sup> have studied the kinetics of the formation of the blue peroxychromate,  $\text{CrO}_5 \cdot \text{H}_2\text{O}$ , and have reported the following rate expression for the reaction:

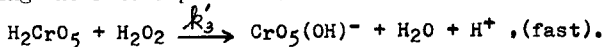
$$\begin{aligned} d[\text{CrO}_5 \cdot \text{H}_2\text{O}]/dt &= k[\text{HCrO}_4^-][\text{H}^+][\text{H}_2\text{O}_2] \\ k &= 107.6 \pm 0.2 \exp(-4500 \text{ cal}/RT) \end{aligned}$$

The reaction, which occurs under more acidic conditions than does the formation of  $\text{HCrO}_6^-$ , may proceed by the following mechanism:



The observed rate constant,  $k$ , would be equal to  $k_2K_B$ .

Since the formation of the violet peroxychromate proceeds according to an identical rate expression, it is likely that the corresponding mechanism is similar to that presented above. In fact, a simple modification of the last step, which reflects the less acidic conditions under which  $\text{HCrO}_6^-$  is produced, yields the violet species without changing the rate expression.



According to this mechanism, the observed  $k$  would still be equal to  $k_2K_B$ . This suggests that the rate constants for formation of the blue and violet species should be the same. Comparison of Wilkins' et al expression for  $k_{\text{blue}}$  above,

with our violet,

$$k_{\text{violet}} = 10^{7.9} \exp(-5100 \text{ cal/RT}).$$

confirms our expectations. It appears, therefore, that, except for the fast third step, the formation of the blue and violet perchromates proceed via a common mechanism.



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