

Figure 1. Sample run of the oxidation of CHT with chromic acid.

Table II. Determination of the Isotope Effect of Cycloheptatriene with Chromic Acid

Substrate	Concn, $\times 10^{-2} M$	$10^2 k_2, M^{-1} \text{sec}^{-1}$	Av	$k_H/k_D$
CHT	5.37	2.82	2.85	0.98
	5.58	2.84		
	5.81	2.92		
CHT- $d_8$	4.48	3.04	2.90	
	4.33	2.73		
	6.20	2.97		

A mixture containing CHT and CHT- $d_2$  in ca. 30 ml of 90% acetic acid (757 mg) was oxidized for 3 hr with 772 mg of potassium dichromate at room temperature. The volatile part of the solution was distilled on a vacuum line. A known amount of ethanol was added as standard, and the amount of recovered CHT (515 mg) was determined by glpc. The solution was then diluted with water. CHT was extracted with ether and purified by preparative glpc. The isotopic composition of the CHT before and after the oxidation

was determined by low-voltage mass spectrometry. The initial mixture had peaks at  $m/e$  92 (46.3%), 93 (9.1%), and 94 (44.6%), the values representing the average of nine measurements with a standard deviation of  $\pm 0.2$ . After correction for  $^{13}\text{C}$  the composition is 48.3, 5.7, and 46.0%. The peak at  $m/e$  91 had an intensity below 2% and could not be determined precisely owing to the small signal/noise ratio. No correction was therefore applied for fragmentation of the CHT. The composition of the recovered CHT (two measurements) was 41.3, 10.2, and 48.5%. (A third determination with 41.2, 9.3, and 49.5% was not included in the calculation.) After correction for  $^{13}\text{C}$  the composition was 42.8, 7.3, and 49.8%. For the computation of the CHT a correction for a toluene impurity was applied (4% in the CHT- $d_2$  before and 5% after the reaction). Accordingly the initial CHT mixture contained 362 mg of CHT, 339 mg of CHT- $d_2$ , and 41 mg of CHT- $d$ . The recovered CHT was composed of 218 mg of CHT, 248.5 mg of CHT- $d_2$ , and 36 mg of CHT- $d$ . The isotope effect was calculated with

$$k_H/k_D = \frac{\log \{ \text{CHT}_E / \text{CHT}_0 \}}{\log \{ d_2\text{-CHT}_E / d_2\text{-CHT}_0 \}} = 1.61 \pm 0.2 \quad (1)$$

The indices E and 0 correspond to the concentrations at the end and at the beginning of the reaction. The applicability of eq 1 requires that the reaction rate of CHT- $d$  ( $k_{HD}$ ) =  $1/2 k_{HH} + 1/2 k_{DD}$ . The experimental error is estimated from the error in the mass spectra (5.5%) and from the determination of the CHT (2%). To this is added a systematic error of 5% for systematic errors, such as baseline error and potential loss of CHT during the vacuum line distillation.

**Isotope Effect with Triphenylmethyl Perchlorate.** A mixture of CHT (122 mg), CHT- $d_2$  (112 mg), and CHT- $d$  (16 mg) in 5 ml of dry acetonitrile was reacted with 177 mg of triphenylmethyl perchlorate.<sup>35</sup> After 5 min the flask was frozen with liquid nitrogen and the volatile components were removed by bulb-to-bulb distillation. The residue was extracted with ether to yield, after evaporation and sublimation, 113.6 mg (0.46 mmol) of triphenylmethane, mp 92°. The volatile fraction consisted of 93.5 mg of unreacted CHT and 107.5 mg of CHT- $d_2$  as calculated from the isotopic composition of the isolated triphenylmethane (24.9% monodeuterio compound). Calculation as above gave  $k_H/k_D = 2.95 \pm 0.2$ .

**Acknowledgments.** The authors are indebted to Professor K. Rinehart, University of Illinois at Urbana-Champaign, for mass spectral measurements.

(35) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

## Chromium(IV) Oxidation of Aromatic Aldehydes

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**Abstract:** The previously introduced method for the study of chromium(IV) oxidations in which chromium(IV) is generated *in situ* in the course of the reduction of chromium(VI) by vanadium(IV) was adapted for use with water-insoluble substrates. The chromium(IV) oxidation of substituted aromatic aldehydes gave a value of  $\rho = +0.97$ . A mechanism consisting of a rate-limiting decomposition of a chromium(IV) complex of the aldehyde hydrate is proposed. The results permitted the recalculation of the  $\rho$  value for the chromium(V) oxidation of aromatic aldehydes using results obtained earlier by Wiberg and Richardson; a value of  $\rho = +0.30$  was obtained.

The chromium(VI) oxidation of vanadium(IV) in the aqueous system has been extensively studied by Espenson, who showed that the reaction followed Scheme I.<sup>1</sup> We have previously employed this system successfully in the study of the chromium(IV) oxidation of alcohols,<sup>2,3</sup> aliphatic aldehydes,<sup>4</sup> and oxalic acid.<sup>5</sup>

(1) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964).

(2) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); **95**, 7123 (1973).

However, our studies thus far have been confined to the aqueous system in which a great many organic compounds have only limited solubility.

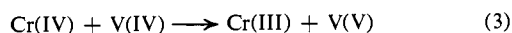
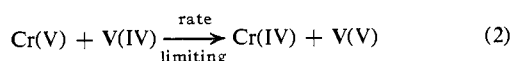
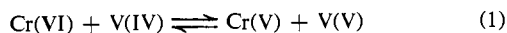
The purpose of this work was to develop a method which would permit the study of chromium(IV) oxidations of water-insoluble substrates. We found that

(3) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

(4) J. Roček and C. S. Ng, *J. Amer. Chem. Soc.*, **96**, 1522 (1974).

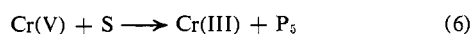
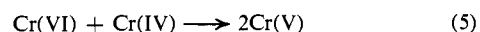
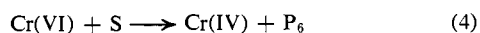
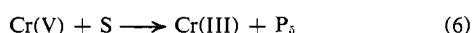
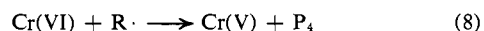
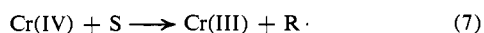
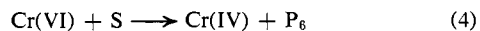
(5) F. Hasan and J. Roček, *Tetrahedron*, in press.

## Scheme I



organic substrates and the required vanadium and chromium compounds are sufficiently soluble in 70% acetic acid, and therefore selected this solvent for all studies reported in this paper. Before attempting to investigate chromium(IV) oxidation of organic compounds in this medium, the effect of the change in solvent on the reaction between chromic acid and vanadium(IV) had to be established. It further seemed desirable to reexamine in some detail a previously investigated substrate, isopropyl alcohol, in the new solvent system in order to test the method and gain confidence in the results.

To demonstrate the applicability of our approach to the investigation of chromium(IV) oxidations to water-insoluble compounds, we selected a series of aromatic aldehydes. For years, the only major work on the oxidation of aromatic aldehydes by the intermediate valence chromium species has been that by Wiberg and Richardson,<sup>6</sup> who studied the competitive oxidation of pairs of aromatic aldehydes by chromic acid in 91% acetic acid. They discussed the results in terms of two different mechanisms (Schemes II and III), of which the first seemed more likely at that time.

Scheme II<sup>7</sup>Scheme III<sup>7</sup>

Based on mechanism II, a value of +0.45 was obtained for the Hammett  $\rho$  constant for the chromium(V) oxidation.

Recent studies have shown that chromium(IV) is a highly reactive oxidant, not only in aqueous solutions,<sup>2-5,8</sup> but also in aqueous acetic acid.<sup>9,10</sup> These findings, as well as thermodynamic considerations<sup>11</sup> make Scheme III more attractive.

In order to calculate a value for the  $\rho$  constant for mechanism III, Wiberg and Richardson had to make a guess about the value of the  $\rho$  constant for the chromium(IV) oxidation. Based on known  $\rho$  constants for the autoxidation of aromatic aldehydes and of other hydrogen atom abstraction reactions, they proposed that the value of the  $\rho$  constants should be within the

(6) K. B. Wiberg and W. H. Richardson, *J. Amer. Chem. Soc.*, **84**, 2800 (1962).

(7)  $\text{P}_6$ ,  $\text{P}_5$ , and  $\text{P}_4$  refer to oxidation products resulting from the initial interaction of the substrate with chromium(VI), chromium(V), and chromium(IV), respectively.

(8) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5462 (1971).

(9) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 1120 (1970); **93**, 4536 (1971).

(10) K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **93**, 2543 (1971).

(11) E. A. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 5890 (1965).

range of -0.5 to -1.0. This choice led to a range of +1.6 to +2.2 for the chromium(V) oxidation. However, later work on the oxidation of aldehydes seemed to suggest that the  $\rho$  constants could have a positive rather than a negative value. *E.g.*, Cooper and Waters<sup>12</sup> found that electron-withdrawing substituents accelerate the cobalt(III) oxidation of aromatic aldehydes in aqueous acetonitrile.

The approach employed in this work permits a distinction between mechanisms II and III, an experimental determination of the value of the  $\rho$  constant for the chromium(IV) oxidation, and, in combination with the earlier results of Wiberg and Richardson, a recomputation of the  $\rho$  constant for the chromium(V) oxidation.

## Experimental Section

**Materials.** Benzaldehyde (Mallinckrodt Chemicals), *p*-tolu-aldehyde, *m*-tolu-aldehyde, *m*-chlorobenzaldehyde, *p*-anisaldehyde, and *m*-anisaldehyde (all from Aldrich Chemicals) were checked for purity by glpc. Impure samples were first purified by distillation through a 14-cm silvered vacuum-jacketed column packed with Nichrome Halipak in a nitrogen atmosphere. The pure samples (checked by glpc) were distilled through a Vigreux column under a vacuum of about 0.1 mm with a fine stream of nitrogen flowing through the system.<sup>13</sup> Solutions of the aldehydes in 70% aqueous acetic acid were prepared inside an inert atmosphere box.

*p*-Nitrobenzaldehyde (Baker Chemicals), *m*-nitrobenzaldehyde (Matheson Coleman and Bell), and *p*-cyanobenzaldehyde (City Chemicals) were purified by recrystallization from water-ethanol mixture, followed by sublimation under vacuum. Their purity was checked by melting point determination.

*p*-Chlorobenzaldehyde (City Chemicals) was purified in a manner similar to that described for the liquid aldehydes, except that water at 70° was circulating through the condenser. Purity was checked by melting point determination and by glpc.

Isopropyl alcohol (Baker Chemicals), shown to be pure by glpc, was used without further purification.

Vanadyl sulfate and vanadium pentoxide were Fisher reagents; lithium and barium perchlorates were from G. F. Smith Co.; perchloric acid was 72% reagent from Baker and Adamson. A.R. potassium dichromate was used without further purification.

Vanadium(IV) perchlorate solution was prepared by reacting vanadyl sulfate with barium perchlorate using the method of Espenson.<sup>1</sup> Solutions of vanadium(V) perchlorate were prepared by stirring vanadium pentoxide in perchloric acid overnight. The concentrations of vanadium(IV), vanadium(V), and chromium(VI) solutions were determined spectrophotometrically.<sup>1</sup>

Commercial reagent grade acetic acid (Fisher Scientific) contained impurities gradually oxidized by chromic acid. It had to be specially purified when used as a solvent in chromic acid oxidation studies. The purification procedures were as follows. The acetic acid was refluxed with 5% potassium permanganate (Baker Chemicals) by weight for about 5 hr and the resultant acid was distilled twice under partial vacuum (*ca.* 20 cm) using a 30-cm Vigreux column. The double-distilled acetic acid was further distilled at atmospheric pressure through a 40-cm silvered vacuum-jacketed column packed with glass helices and fitted to a distillation head with reflux control. The fraction at 115-117° was collected.

**Molar Absorptivities of Chromium(VI), Chromium(III), Vanadium(IV), and Vanadium(V) in 70% (v/v) Aqueous Acetic Acid.** The molar absorptivities of the above inorganic species in aqueous acetic acid were determined at 350 and 764 nm using Lambert-Beer's law. The absorbance of solutions containing various known amounts of the inorganic species in question was determined at the respective wavelengths. The molar absorptivity was calculated from the slope of the plot of absorbance *vs.* concentration. At 764 nm, chromium(VI), chromium(III), and vanadium(V) were found to be essentially transparent. For vanadium(IV), the molar absorptivity  $\epsilon$  was found to be  $22.6 \pm 0.01$  in 0.004-0.04 *M* of  $\text{HClO}_4$ . Vanadium(IV) was found to be practically transparent at

(12) T. A. Cooper and W. A. Waters, *J. Chem. Soc.*, 1538 (1964).

(13) For details, *cf.* C. S. Ng, Ph.D. Thesis, University of Illinois at Chicago Circle, 1973.

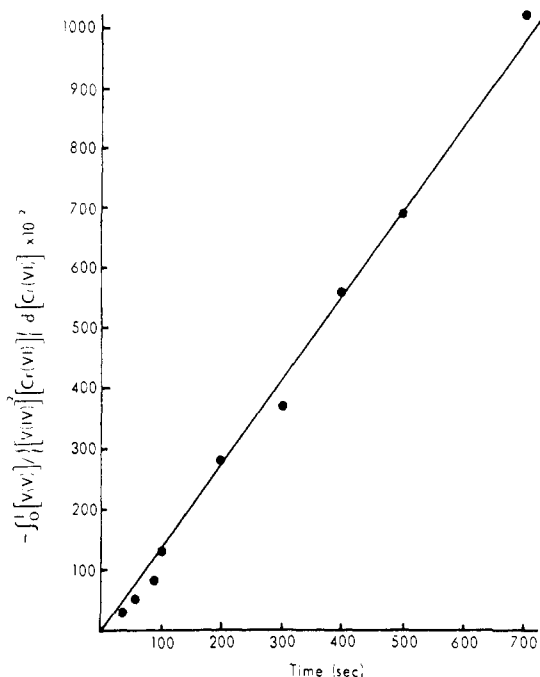


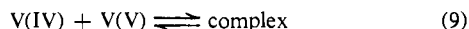
Figure 1. Plot of the integrated rate expression (eq 10) of the chromium(VI)-vanadium(IV) reaction in 70% (v/v) aqueous acetic acid at 25° in 0.0048 M HClO<sub>4</sub>; [LiClO<sub>4</sub>] = 2.0 × 10<sup>-1</sup> M. Initial concentrations: [Cr(VI)] = 9.12 × 10<sup>-6</sup> M, [V(IV)] = 4.40 × 10<sup>-5</sup> M, [V(V)] = 3.47 × 10<sup>-7</sup> M.

Table I. Molar Absorptivities at 350 nm in 70% Aqueous Acetic Acid ([HClO<sub>4</sub>] = 0.004 M)

	ε
Chromium(VI)	950 ± 5.5
Chromium(III)	3.36 ± 0.02
Vanadium(V)	123.2 ± 0.2
Vanadium(IV)	0.0

350 nm. The molar absorptivities at 350 nm are shown in Table I; vanadium(IV) was practically transparent.

**Interaction of the Inorganic Species in 70% Aqueous Acetic Acid.** Experiments were carried out to determine if there were any interaction at 350 and 764 nm of the following pairs in the aqueous acetic acid system: vanadium(V)-chromium(VI), chromium(VI)-chromium(III), chromium(III)-vanadium(V), chromium(III)-vanadium(IV), and vanadium(IV)-vanadium(V). The experiments consisted of comparing absorbances of a two-component system with the sum of the absorbances of the two separate components. At 350 nm, and at concentrations of vanadium(V) ~10<sup>-5</sup> M, vanadium(IV) ~10<sup>-5</sup> M, chromium(VI) ~10<sup>-6</sup> M, and chromium(III) ~10<sup>-6</sup> M, no significant interaction could be detected. At 764 nm and at about 10<sup>-3</sup> M concentrations, the only pair that showed significant interaction was vanadium(IV)-vanadium(V). It was shown that the interaction was due to the formation of a 1:1 complex between vanadium(IV) and vanadium(V) (eq 9) with an equilibrium



constant of 2240 M<sup>-1</sup> and a molar absorptivity ε(764 nm) = 35.4 which is 57% higher than the absorptivity of vanadium(IV) alone.<sup>13</sup> All measurements were carried out in 0.004 M perchloric acid.

**Kinetics of the Chromium(VI) and Vanadium(V) Oxidation of Isopropyl Alcohol.** Kinetics measurements were made by following the decrease in the concentration of the oxidant spectrophotometrically at 350 nm using a Cary Model 15 double beam spectrophotometer. The reactions were carried out at 25° in 70% (v/v) aqueous acetic acid at 0.006 M perchloric acid. Pseudo-first-order rate constants were determined graphically.

**Kinetic Measurements of the Chromium(VI)-Vanadium(IV) System in 70% Acetic Acid.** All the necessary reagents were first

degassed three times and placed in the inert atmosphere box (Vacuum Atmosphere Company Dry-Lab Glove Box Model HE 43-2 with HE 463 Dry Train containing molecular sieve). A solution in 70% aqueous acetic acid containing vanadium(IV), vanadium(V), lithium perchlorate, perchloric acid, and a variable amount of isopropyl alcohol was prepared in a 50-ml volumetric flask inside the box. The solution (25 ml) was pipetted into a 10-cm silica cell; the cell was tightly closed with a rubber septum, taken out of the inert atmosphere box, and equilibrated at 25° for 20 min in the cell compartment of the Cary 15 spectrophotometer. A known amount of chromium(VI) was introduced with a syringe, and the absorbance at 350 nm was followed with time. In a typical experiment, the initial concentrations of the reagents were as follows: [V(IV)]<sub>0</sub> = 4.40 × 10<sup>-5</sup> M, [V(V)]<sub>0</sub> = 3.47 × 10<sup>-7</sup> M, [Cr(VI)]<sub>0</sub> = 9.16 × 10<sup>-6</sup> M, [HClO<sub>4</sub>] = 4.76 × 10<sup>-3</sup> M, [LiClO<sub>4</sub>] = 2.0 × 10<sup>-1</sup> M, [iPrOH]<sub>0</sub> = 1.27 × 10<sup>-3</sup> M. Rate constants were obtained from the slope of plots  $-\int_0^t \frac{d[\text{Cr(VI)}]}{[\text{Cr(VI)}]} \frac{d[\text{V(V)}]}{[\text{V(V)}]^2}$  vs. time.<sup>3</sup> A typical kinetic plot is shown in Figure 1.

In aqueous acetic acid, the chromium(VI) oxidation of vanadium(IV) occurs very rapidly (about 200 times faster than the same reaction in water). Hence the concentration of the reagents involved had to be reduced considerably (in comparison with studies in aqueous solutions) in order to follow the reaction.

**Yield of Vanadium(V) in the Oxidation of Vanadium(IV) by Chromium(VI) in the Absence and Presence of Organic Substrates.** All oxidations were done inside the inert atmosphere box. Solutions of the inorganic reagents, water, glacial acetic acid, and aqueous acetic acid were first degassed and placed in the box. Required amounts of vanadium(IV), vanadium(V), perchloric acid, glacial acetic acid, aldehyde solution in 70% aqueous acetic acid, and chromium(VI) were mixed and diluted to 25 ml with 70% aqueous acetic acid in a volumetric flask. After mixing the solution thoroughly, it was transferred to a 10-cm cylindrical silica cell and taken out of the inert atmosphere box. The absorbance at 764 nm was determined using the Cary 15 spectrophotometer. In one set of data, five to six such runs were made, with different concentration of the aldehyde. In the determination for *p*-tolualdehyde, for example, the oxidation mixture contained 0.0432 mmol of V(IV), *p*-tolualdehyde (0, 5.48, 13.7, 27.4, and 41.4 mmol, respectively), and 0.01 mmol of Cr(VI) in 25 ml of 0.004 M HClO<sub>4</sub> in 70% aqueous acetic acid. The last two mixtures also contained 0.0095 mmol of V(V). The added vanadium(V) was used to prevent the dimerization of the organic radicals which occurred as a side reaction at high initial aldehyde concentration.<sup>3</sup>

## Results and Discussion

**Chromic Acid Oxidation of Vanadium(IV) in 70% Acetic Acid.** Figure 1 gives an example of a plot based on the integrated form of the rate law<sup>1,3</sup> (eq 10) de-

$$-d[\text{Cr(VI)}]/dt = k_{\text{expt}}[\text{Cr(VI)}][\text{V(IV)}]^2/[\text{V(V)}] \quad (10)$$

rived from the mechanism established in aqueous solutions and given in Scheme I. The good straight line plots indicated that the reaction follows the same rate law in both solvents. It is therefore reasonable to assume that the mechanism established by Espenson<sup>1</sup> for aqueous solutions is also valid in 70% acetic acid.

The rate of the reaction in acetic acid solution is about 200 times higher than in water. In this respect, the oxidation of vanadium(IV) resembles the chromic acid oxidation of alcohols,<sup>14,15</sup> hydrocarbons,<sup>16,17</sup> and carboxylic acids,<sup>18</sup> all of which exhibit a strong solvent dependence and are much faster in acetic acid than in water.

(14) M. Cohen and F. W. Westheimer, *J. Amer. Chem. Soc.*, **74**, 4387 (1952).

(15) J. Roček, F. H. Westheimer, A. Eschenmoser, L. Moldoványi, and J. Schreiber, *Helv. Chim. Acta*, **45**, 2554 (1962).

(16) J. Roček and F. Šorm, *Collect. Czech. Chem. Commun.*, **20**, 1001 (1955).

(17) J. Roček, *Collect. Czech. Chem. Commun.*, **22**, 1509, 1519 (1957).

(18) F. Mareš and J. Roček, *Collect. Czech. Chem. Commun.*, **26**, 2389 (1961).

The large increase in the overall reaction rate in the chromic acid oxidation of vanadium(IV) may be due either to an effect of the solvent change on the position of the equilibrium between chromium(VI) and chromium(V) (reaction 1) or to an increase in the rate of the chromium(V) oxidation of vanadium(IV) (reaction 2). The latter interpretation is in agreement with several recent indications of a close similarity between oxidative properties of chromium(VI) and chromium(V).<sup>19-21</sup>

**Induced Oxidation of Isopropyl Alcohol.** The rate constant for the chromium(VI) oxidation of isopropyl alcohol in 70% acetic acid and 0.006 M perchloric acid is  $1.09 \times 10^{-3} M^{-1} \text{sec}^{-1}$ . Under the same condition, the oxidation of the alcohol by vanadium(V) is too slow to measure, while the rate constant for the chromium(VI) oxidation of vanadium(IV) is over 100  $M^{-1} \text{sec}^{-1}$  (Table II). Hence, no direct oxidation by either chromium(VI) or vanadium(V) will take place if isopropyl alcohol is introduced into the chromium(VI)-vanadium(IV) system. The reduction in the yield of vanadium(V) (Figure 2) therefore indicates that a chromium(IV) or chromium(V) oxidation of the alcohol takes place. The results given in Table II show

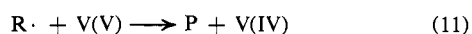
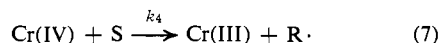
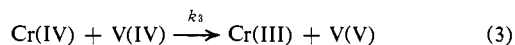
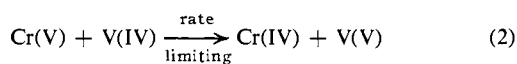
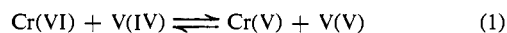
Table II. Kinetics<sup>a</sup> of the Chromic Acid Oxidation of Vanadium(IV) in 70% (v/v) Aqueous Acetic Acid in the Presence of Isopropyl Alcohol at 25°

$[(\text{CH}_3)_2\text{CHOH}], M$	$k_{\text{exptl}}, M^{-1} \text{sec}^{-1}$
0	111
0	143
0	124
0.00127	144
0.00634	127
0.0127	130
0.0254	150

<sup>a</sup>  $[\text{HClO}_4] = 0.0048 M$ ; initial concentrations:  $[\text{V(IV)}] = 4.40 \times 10^{-5} M$ ,  $[\text{V(V)}] = 3.47 \times 10^{-7} M$ ,  $[\text{Cr(VI)}] = 8.2-9.4 \times 10^{-6} M$ .

that the presence of isopropyl alcohol has little effect on the overall rate of the reduction of chromic acid. This requires that the oxidation of the alcohol takes place after the rate-limiting step and leads to the conclusion that the reaction in this solvent follows the same mechanism (Scheme IV) as previously established for

#### Scheme IV



aqueous solutions,<sup>3</sup> and involves a chromium(IV) oxidation of the alcohol.

**Relative Reactivity of the Chromium(IV) Oxidation of Aromatic Aldehydes.** The relative rates of the chromium(IV) oxidation of aromatic aldehydes were obtained from the yields of the vanadium(V) in the

(19) K. B. Wiberg and H. Schaefer, *J. Amer. Chem. Soc.*, **91**, 933 (1969).

(20) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **96**, 534 (1974).

(21) V. Srinivasan and J. Roček, *J. Amer. Chem. Soc.*, **96**, 127 (1974).

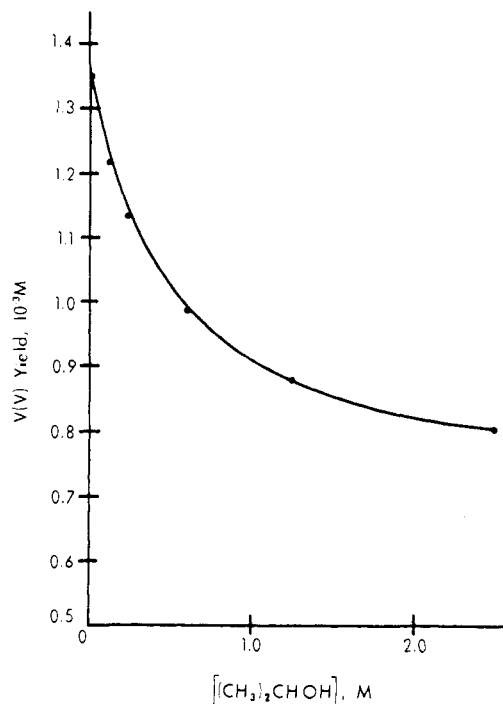


Figure 2. Effect of isopropyl alcohol concentration in the yield of vanadium(V), 0.004 M  $\text{HClO}_4$  in 70% aqueous acetic acid at 25°. Initial concentrations:  $[\text{V(IV)}] = 1.74 \times 10^{-5} M$ ,  $[\text{Cr(VI)}] = 4.4 \times 10^{-6} M$ .

chromium(VI)-vanadium(IV) system.<sup>3,4</sup> A complication arose when the reaction was run in aqueous acetic acid due to the complex formation between vanadium(IV) and vanadium(V). Equations 12-15 are

$$[\text{V(V)}] = \frac{l\epsilon_0 K[\text{V}]_T - 2KA - l\epsilon_4 + [(l\epsilon_0 K[\text{V}]_T - 2KA - l\epsilon_4)^2 + 4lK\epsilon_0(l\epsilon_4[\text{V}]_T - A)]^{1/2}}{2l\epsilon_0 K} \quad (12)$$

$$[\text{V(IV)}] = \frac{A}{l\{\epsilon_4 + K\epsilon_0[\text{V(V)}]\}} \quad (13)$$

$$[\text{C}] = K[\text{V(IV)}][\text{V(V)}] \quad (14)$$

$$[\text{V(V)}]_T = [\text{V(V)}] + [\text{C}] \quad (15)$$

where

$A$  = absorbance at 764 nm

$l$  = length of the spectrophotometer cell (10 cm)

$\epsilon_4$  = molar absorptivity of V(IV) (22.6)

$\epsilon_0$  = molar absorptivity of V(IV)-V(V) complex (35.4)

$K$  = equilibrium constant for the formation of V(IV)-V(V) complex ( $= 2240 M^{-1}$ )

$[\text{V(V)}]$  = concentration of free V(V)

$[\text{V(IV)}]$  = concentration of free V(IV)

$[\text{C}]$  = concentration of complex

$[\text{V}]_T = [\text{V(IV)}] + [\text{V(V)}] + 2[\text{C}] = \text{total concentration of vanadium}$

used to calculate the yield of vanadium(V),  $[\text{V(V)}]_T$ , from the experimental values of the absorbance at 764 nm.<sup>13</sup> The relative rate of the oxidation is then obtained from the slope of the plot  $([\text{V(V)}]_T)_{\text{max}} - [\text{V(V)}]_T / ([\text{V(V)}]_T - 0.33 [\text{V(V)}]_{T,\text{max}})$  vs.  $[\text{S}] / [\text{V(IV)}]_{\text{av}}$ .<sup>3,4</sup> Figure 3 shows such a plot for the oxidation of *p*-tolualdehyde.

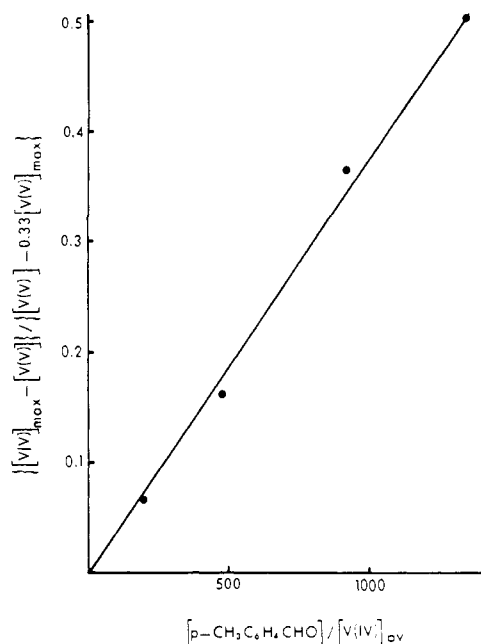


Figure 3. Effect of *p*-tolualdehyde on the yield of vanadium(V) in 70% aqueous acetic acid and 0.004 M HClO<sub>4</sub> at 25°. Initial concentrations: [V(IV)] = 1.73 × 10<sup>-3</sup> M, [Cr(VI)] = 4.4 × 10<sup>-4</sup> M.

Table III. Chromium(IV) Oxidations of Aromatic Aldehydes<sup>a</sup>

Substrate	$\sigma^b$	$10^3 k_4/k_3^c$	$k/k_{\text{C}_6\text{H}_5\text{CHO}}$
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	-0.27	1.17 ± 0.17	2.65
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	-0.17	0.342 ± 0.025	0.774
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	-0.07	0.358 ± 0.006	0.810
C <sub>6</sub> H <sub>5</sub> CHO	0	0.442 ± 0.002	1.00
<i>m</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	+0.115	0.505 ± 0.049	1.14
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	+0.23	0.553 ± 0.066	1.25
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	+0.37	0.635 ± 0.014	1.44
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub> CHO	+0.66	1.60 ± 0.14	3.62
<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	+0.71	2.05 ± 0.35	4.64
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	+0.78	3.20 ± 0.17	7.24
CH <sub>3</sub> CH <sub>2</sub> CHO <sup>d</sup>		2.08 ± 0.014 <sup>e</sup>	4.71
(CH <sub>3</sub> ) <sub>2</sub> CHOH <sup>d</sup>		1.52 ± 0.17	3.44
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH <sup>d</sup>		37.9 ± 4.5	85.7

<sup>a</sup> Solvent: 70% (v/v) aqueous acetic acid. <sup>b</sup> Reference 29. <sup>c</sup> Cf. Scheme IV. <sup>d</sup> Included for comparison. <sup>e</sup> This value was calculated on the basis of the total analytical concentration of the aldehyde.

Table III summarizes the data of the relative reactivity of aromatic aldehydes toward chromium(IV). It also gives the data for isopropyl alcohol, benzyl alcohol, and propionaldehyde for comparison. A Hammett  $\sigma\rho$  plot for the aromatic aldehydes is shown in Figure 4. The value of the reaction constant,  $\rho$ , was calculated from the slope of the plot to be +0.97, with a correlation coefficient of 0.97 and a standard deviation of 0.098. In the calculation of the reaction constant, the value of *p*-anisaldehyde was ignored, since it was possible that this aldehyde reacted by a mechanism different from that of the other aldehydes. It has been pointed out that the *p*-methoxy group activates the benzene ring to such an extent that direct attack on the aromatic nucleus is possible.<sup>22</sup> An anomalous result for the *p*-methoxy group was also obtained by Trahanovsky, who found that 2-(*p*-methoxyphenyl)-1-

(22) H. C. Duffin and R. B. Tucker, *Tetrahedron*, **23**, 2803 (1967).

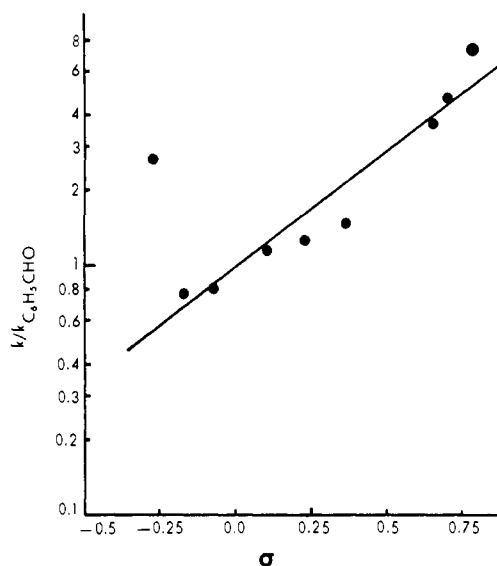


Figure 4. Hammett plot of chromium(IV) oxidation rates for aromatic aldehydes.

phenylethanol was oxidized at least 100–1000 times faster than 2-(*p*-methylphenyl)-1-phenylethanol by cerium(IV), while the rate of the cerium(IV) oxidation of 2-(methylphenyl)-1-phenylethanol relative to that of 2-phenyl-1-phenylethanol was only 4.2.<sup>9</sup>

The result obtained in this study thus differs in sign from the value which was assumed from this reaction by earlier investigators,<sup>6</sup> as well as from the experimental values determined for the reaction of aldehydes with nitrogen dioxide in benzene ( $\rho = -1.1$ ),<sup>23</sup> with trichloromethyl radicals in carbon tetrachloride ( $\rho = -0.74$ ),<sup>24a</sup> with trichloromethanesulfonyl radicals ( $\rho = -0.54$ ),<sup>24b</sup> sulfur chloride ( $\rho = -0.53$ ),<sup>24c</sup> and with perbenzoate radicals in acetic anhydride ( $\rho = -0.49$ ).<sup>25</sup> On the other hand, it is quite similar to the value obtained by Wiberg<sup>6, 28</sup> for the chromium(VI) oxidation in 91% aqueous acetic acid, and thus suggests that the mechanisms of the chromium(IV) and chromium(VI) oxidations of aromatic aldehydes are closely related.

It should be noted that the  $\rho$  value of +0.97 for aromatic aldehydes is based on the total concentration of the aldehyde. As the extent of hydration of aromatic aldehydes is generally believed to be extremely small, this value also represents the  $\rho$  value for the oxidation of the free aldehyde. It is similar to the  $\rho^*$  value obtained in the chromium(IV) oxidation of aliphatic aldehydes based on the concentration of the free aldehyde (+0.72),<sup>4</sup> and suggests that the chromium(IV) oxidations of the aliphatic and aromatic aldehydes follow a similar course. We therefore believe that a hydrate or hydrate-like intermediate is involved in both cases. Additional support for this conclusion can be obtained from the analysis of relative oxidation rates of aliphatic and aromatic aldehydes and alcohols. Aliphatic aldehydes, which are hydrated to a con-

(23) T. Yoshida and K. Namba, *Kogyo Kagaku*, **29**, 353 (1968).

(24) (a) K. H. Lee, *Tetrahedron*, **24**, 4793 (1968); (b) *ibid.*, **26**, 1503 (1970); (c) *ibid.*, **26**, 2041 (1970).

(25) Calculated by Jaffe<sup>26</sup> from data obtained by Walling and McElhill.<sup>27</sup>

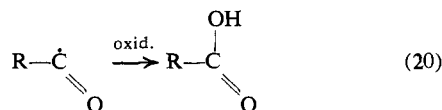
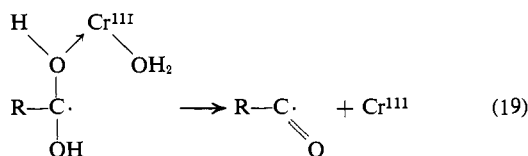
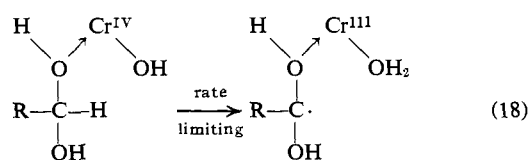
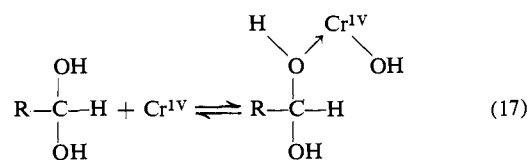
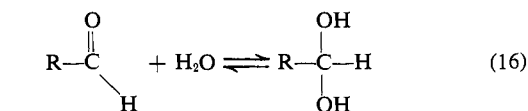
(26) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(27) C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.*, **73**, 2927 (1951).

(28) K. B. Wiberg and T. Mill, *J. Amer. Chem. Soc.*, **80**, 3022 (1958).

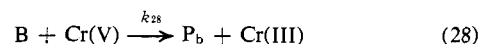
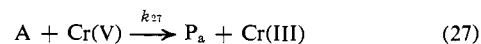
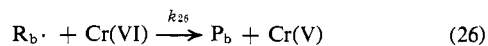
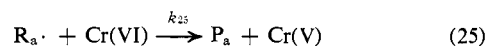
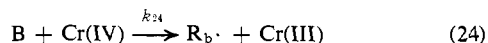
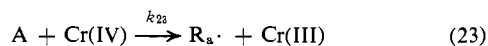
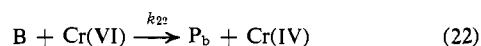
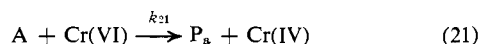
siderable extent, react at comparable rates as the corresponding alcohols.<sup>3,4</sup> On the other hand, benzaldehyde is 85 times less reactive than benzyl alcohol (Table III), indicating that the lower ability of benzaldehyde to form a hydrate or a hydrate-like intermediate results in a lowered reactivity. We therefore propose that the chromium(IV) oxidation of aromatic aldehydes follows the same mechanism that we have proposed for the oxidation of aliphatic aldehydes<sup>4</sup> (Scheme V).

Scheme V



**Relative Reactivity of Aromatic Aldehydes toward Chromium(V).** In their investigation on the oxidation of aromatic aldehydes by intermediate chromium species, Wiberg and Richardson obtained data on the competitive oxidation of several pairs of aldehydes by chromic acid.<sup>6</sup> Combining these data and our own data on the chromium(IV) oxidation of aldehydes, and following Wiberg's method of deduction, one can estimate the relative reactivity of aromatic aldehydes

Scheme IIIa



$$-d[\text{A}]/dt = k_{21}[\text{A}][\text{Cr(VI)}] + k_{23}[\text{A}][\text{Cr(IV)}] + k_{27}[\text{A}][\text{Cr(V)}] \quad (29)$$

$$-d[\text{B}]/dt = k_{22}[\text{B}][\text{Cr(VI)}] + k_{24}[\text{B}][\text{Cr(IV)}] + k_{28}[\text{B}][\text{Cr(V)}] \quad (30)$$

toward chromium(V), assuming that the chromic acid oxidation of aldehydes follows Scheme III.

If Scheme III is followed in the competitive oxidation of a mixture of two aldehydes, A and B, Scheme IIIa may be written for the system. Starting with equal concentrations of A and B, at time 0, the steady-state concentrations of the intermediates are given by

$$[\text{Cr(IV)}] = \frac{(k_{21} + k_{22})[\text{Cr(VI)}]}{k_{23} + k_{24}} \quad (31)$$

$$[\text{R}_a \cdot] = \frac{k_{23}[\text{A}](k_{21} + k_{22})}{k_{25}k_{23} + k_{24}} \quad (32)$$

$$[\text{R}_b \cdot] = \frac{k_{24}[\text{B}](k_{21} + k_{22})}{k_{26}k_{23} + k_{24}} \quad (33)$$

$$[\text{Cr(V)}] = \frac{[\text{Cr(VI)}](k_{21} + k_{22})}{k_{27} + k_{28}} \quad (34)$$

Upon substitution of eq 31 and eq 34 for [Cr(IV)] and [Cr(V)] respectively into eq 29 and eq 30

$$-\frac{d[\text{A}]}{dt} = k_{21}[\text{A}][\text{Cr(VI)}] + \frac{k_{23}[\text{A}][\text{Cr(VI)}](k_{21} + k_{22})}{k_{23} + k_{24}} + \frac{k_{27}[\text{A}][\text{Cr(VI)}](k_{21} + k_{22})}{k_{27} + k_{28}} \quad (35)$$

$$-\frac{d[\text{B}]}{dt} = k_{22}[\text{B}][\text{Cr(VI)}] + \frac{k_{24}[\text{B}][\text{Cr(VI)}](k_{21} + k_{22})}{k_{23} + k_{24}} + \frac{k_{28}[\text{B}][\text{Cr(VI)}](k_{21} + k_{22})}{k_{27} + k_{28}} \quad (36)$$

Dividing eq 35 by eq 36, and rearranging terms

$$\frac{d[\text{A}]}{[\text{A}]} = \frac{d[\text{B}]}{[\text{B}]} \times \frac{\{k_{21} + (k_{21} + k_{22})/(1 + k_{24}/k_{23}) + (k_{21} + k_{22})/(1 + k_{28}/k_{27})\}}{\{k_{22} + (k_{21} + k_{22})/(1 + k_{23}/k_{24}) + (k_{21} + k_{22})/(1 + k_{27}/k_{28})\}} \quad (37)$$

Integrating eq 37 gives

$$\log \frac{A_t}{A_0} = \log \frac{B_t}{B_0} \times \frac{\{k_{21} + (k_{21} + k_{22})/(1 + k_{24}/k_{23}) + (k_{21} + k_{22})/(1 + k_{28}/k_{27})\}}{\{k_{22} + (k_{21} + k_{22})/(1 + k_{23}/k_{24}) + (k_{21} + k_{22})/(1 + k_{27}/k_{28})\}} \quad (38)$$

In eq 38,  $A_0$ ,  $B_0$ ,  $A_t$ , and  $B_t$  are the concentrations of A and B at time 0 and  $t$ , respectively. The rate constants of the chromium(VI) oxidation,  $k_{21}$  and  $k_{22}$ , are available;<sup>28</sup> the relative rate constants for the chromium(IV) oxidation,  $k_{24}/k_{23}$ , were determined in this investigation and are given in the last column of Table III. From the slope of the plot  $\log (A_t/A_0)$  vs.  $\log (B_t/B_0)$ , the relative rate constant of the chromium(V) oxidation,  $k_{28}/k_{27}$ , may be obtained.

Wilberg and Richardson's data<sup>6</sup> on three sets of competitive oxidation by chromic acid are plotted in Figure 5. The slopes of the plots, which give the values of  $\log (A_t/A_0)/\log (B_t/B_0)$ , are given in Table IV, together with the values of  $k_{21}$ ,  $k_{22}$ , and  $k_{23}/k_{24}$ . The values of  $k_{28}/k_{27}$  are calculated using eq 38, and are listed in Table V, which also gives the substituent con-

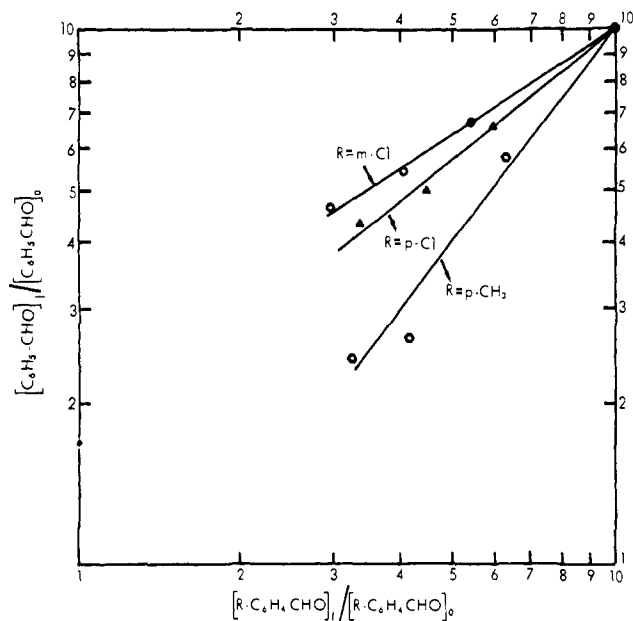


Figure 5. Competitive oxidation of benzaldehyde and substituted benzaldehydes by chromic acid: (○) *m*-chlorobenzaldehyde; (◐) *p*-tolualdehyde; (▲) *p*-chlorobenzaldehyde. Data from ref 6.

Table IV. Data for the Calculation of the Relative Rate of Chromium(V) Oxidation of Aromatic Aldehydes Using Eq 38

	A = C <sub>6</sub> H <sub>5</sub> CHO B = <i>p</i> -Cl- C <sub>6</sub> H <sub>4</sub> CHO	A = C <sub>6</sub> H <sub>5</sub> CHO B = <i>p</i> -CH <sub>3</sub> - C <sub>6</sub> H <sub>4</sub> CHO	A = C <sub>6</sub> H <sub>5</sub> CHO B = <i>m</i> -Cl- C <sub>6</sub> H <sub>4</sub> CHO
$\log(A_i/A_0)/\log(B_i/B_0)^a$	0.791	1.278	0.652
$k_{21}^b, M^{-1} \text{ sec}^{-1}$ (Cr(VI) oxidation of A)	0.00617	0.00617	0.00617
$k_{22}^b, M^{-1} \text{ sec}^{-1}$ (Cr(VI) oxidation of B)	0.00850	0.00426	0.0118
$k_{24}/k_{23}^c$ (rate of Cr(IV) oxidation of B relative to that of A)	1.25	0.774	1.44

<sup>a</sup> From the slopes in Figure 5. <sup>b</sup> Data taken from ref 28. <sup>c</sup> From Table III.

stants of the aldehydes. The relative rates for the chromium(V) oxidation,  $k_{28}/k_{27}$ , are plotted against the  $\rho$  constants.<sup>29</sup> An excellent straight line is obtained (Figure 6). The reaction constant,  $\rho$ , from the slope of the plot, is +0.31, with a correlation coefficient of 1.0 and a standard deviation of 0.0062.

Despite the excellent correlation of the results, it should be emphasized that this  $\rho$  value for the chromium(V) oxidation is only an approximate one, since

(29) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

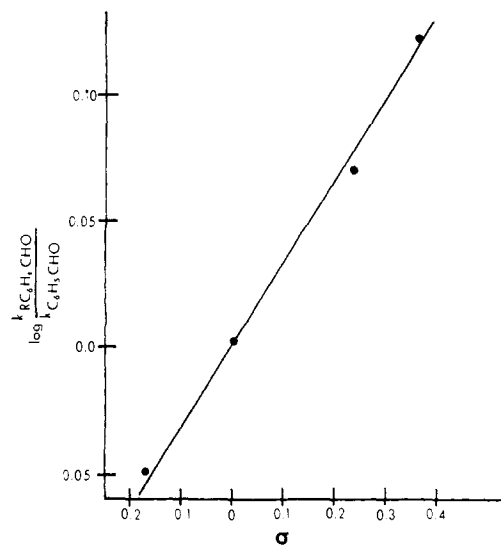


Figure 6. Hammett plot of chromium(V) oxidation rates for aromatic aldehydes.

Table V. Rate of Oxidation of Aromatic Aldehydes Relative to that of Benzaldehyde by Chromium(V)

Aldehyde RC <sub>6</sub> H <sub>4</sub> CHO	$\sigma^a$	$k_{RC_6H_4CHO}/k_{C_6H_5CHO}^b$
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	-0.17	0.893
H-C <sub>6</sub> H <sub>4</sub> CHO	0.0	1.000
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	+0.24	1.171
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	+0.37	1.32

<sup>a</sup> Reference 29. <sup>b</sup> Same as  $k_{28}/k_{27}$  in eq 38.

the results from two different systems (chromium(IV) oxidation in 70% acetic acid, and chromic acid oxidation in 91% acetic acid) are used for the calculation. Nevertheless, this value agrees well with the experimental value of about 0.6 obtained by Wiberg<sup>30</sup> in that they are both small and positive. Since Wiberg's value was obtained by following the reaction of chromium(V) directly, this agreement gives added support that the chromic acid oxidation of aldehydes follows Scheme III. The similarity among the  $\rho$  values for the chromium(VI), chromium(V), and chromium(IV) oxidations of aromatic aldehydes suggests that the three chromium species react with aldehydes *via* similar routes.

**Acknowledgment.** The support of this work by the National Science Foundation is gratefully acknowledged. Computing services provided by the Computer Center of the University of Illinois at Chicago Circle are gratefully acknowledged.

(30) K. B. Wiberg and G. Szeimies, private communications.