

cyclopentadienyltricarbonylcobalt dication,  $C_5H_5Co(CO)_3^{2+}$ , isoelectronic with the  $C_5H_5Co(triphos)^{2+}$  dication remains unknown, possibly owing to insufficient electron density from the cobalt atom in the relatively high formal +3 oxidation state to form the necessary  $d\pi-p\pi$  bonds for stabilization of bonds with three carbonyl groups; the reported<sup>17</sup> monocation  $C_5H_5Co(CO)_2R^+$  with only two carbonyl groups bonded to cobalt(III) is already rather unstable. How-

(17) P. M. Treichel and G. Werber, *Inorg. Chem.*, **4**, 1098 (1965).

ever, the known<sup>18</sup> yellow dication  $C_5H_5CoC_6H_8^{2+}$  is isoelectronic with  $C_5H_5Co(triphos)^{2+}$ . The related dication  $C_5H_5Co(tripy)^{2+}$  has also been prepared from  $C_5H_5Co(CO)I_2$  and 2,2',2''-terpyridyl<sup>18,19</sup> but this material has not been obtained as a completely pure salt.

**Acknowledgment.**—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68.

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CONTRIBUTION FROM LABORATORIO CHIMICA RADIOELEMENTI CNR PADOVA AND ISTITUTO DI CHIMICA ORGANICA INDUSTRIALE, THE UNIVERSITY, BOLOGNA, ITALY

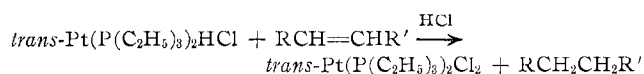
## Reduction of Olefins by Means of an HA-Platinum(II) Hydride System

BY MARIO GIUSTINIANI, GIULIANO DOLCETTI, ROSARIO PIETROPAOLO, AND UMBERTO BELLUCO

Received January 13, 1969

The present work reports on hydrogenation reactions of linear and/or cyclic unsaturated hydrocarbons in the presence of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>HCl and hydrochloric or perchloric (HA) acid in ethanol. Reactions proceed under ambient conditions leading to saturated hydrocarbons and *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The olefins investigated are 1-hexene, cyclohexene, 1-octene, and 2-methyl-2-butene. Electronegatively substituted olefins such as acrylonitrile and *trans*-dichloroethylene do not react under these experimental conditions. The pseudo-first-order rate constants depend upon the concentrations of olefin, mineral acid, and chloride ion. The following conceivable reaction mechanisms are discussed: (i) olefin insertion across the Pt-H bond followed by cleavage of the ensuing platinum(II)-alkyl complex by hydrochloric acid and (ii) formation of a platinum(IV) dihydride with subsequent hydrogenation of the olefin to the corresponding hydrogenated hydrocarbon.

In the present work we report a reduction reaction of linear and cyclic olefins with hydrochloric or perchloric acid in the presence of *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>HCl in ethanol at room temperature. The reactions studied are



where olefin = 1-hexene, cyclohexene, 1-octene, or 2-methyl-2-butene. All of the reactions were carried out in 99.5% ethanol. We established that under the experimental conditions used, the olefins investigated did not react separately with either hydrochloric acid or the platinum hydride. On the other hand, the complex *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>HCl reacts very slowly with HCl yielding Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and molecular hydrogen.<sup>1</sup> We did not succeed in detecting any reaction intermediates. All of the reactions go to completion.

A kinetic investigation has been carried out under pseudo-first-order conditions by using an excess of all other reactants with respect to the metal complex concentration. Values of the pseudo-first-order rate constants,  $k_{\text{obsd}}$  (sec<sup>-1</sup>), at various concentrations of reactants are reported in Table I. Figure 1 shows the plot of  $k_{\text{obsd}}$  vs. LiCl concentration. There is a linear dependence on [Cl<sup>-</sup>] with a nonzero intercept, correspond-

ing to the rate of reaction of the hydride complex with 1-hexene in the presence of perchloric acid alone. Runs 9, 10, and 18 (Table I) show a dependence of the rate on the acid concentration. A wider range of acid concentrations was not examined to avoid the presence of ionic pairs in solution.

These kinetic data indicate that pseudo-first-order rate constants depend on the concentration of mineral acid, chloride ion, and olefin. Although a detailed kinetic investigation of these reactions could not be carried out, we could establish that the reaction rates depend also upon the nature of the olefin. However, we found that the rates of reduction of cyclohexene are of the same order of magnitude as those of 1-hexene.

These olefin reduction reactions display also the following features. (i) No isomerization occurs during the process. In fact, no hexene-2 is formed during the course of a reduction. If isomerization takes place before the material is reduced, it is of no consequence since the final products are the saturated hydrocarbons. (ii) The reduction reactions occur also with cyclohexene and 2-methyl-2-butene, although preparation of secondary alkylplatinum(II) derivatives has always been difficult.<sup>2</sup> (iii) Electronegatively substituted olefins such as acrylonitrile and *trans*-dichloroethylene do not react under the above experimental conditions.

(1) U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.*, **89**, 6494 (1967).

(2) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968), and references therein.

TABLE I  
PSEUDO-FIRST-ORDER RATE CONSTANTS,  $k_{\text{obsd}}$ ,  
IN 99.5% ETHANOL AT 30°<sup>a</sup>

Expt. no.	$trans\text{-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl} + 1\text{-hexene} \xrightarrow{+\text{H}^+, \text{Cl}^-} trans\text{-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2 + n\text{-hexane}$			$10^5 k_{\text{obsd}}$ , sec <sup>-1</sup>
	$10^3 [\text{HClO}_4]$ , M	$10^3 [\text{LiCl}]$ , M	$10^3 [1\text{-hexene}]$ , M	
1	20	20	1.0	1.7
2	20	20	1.5	2.6
3	20	20	3.0	4.3
4	20	20	5.0	5.1
5	20	20	8.0	5.8
6	20	20	12.0	6.5
7	20	20	15.0	6.8
8	20	20	20.0	7.2
9	1	40	200	5.5
10	2	40	200	6.1
11	20	2	200	3.5
12	20	4	200	3.8
13	20	10	200	4.5
14	20	15	200	5.4
15	20	20	200	6.1
16	20	25	200	6.8
17	20	30	200	7.5
18	20	40	200	9.0

<sup>a</sup> Complex concentration *ca.*  $5 \times 10^{-4}$  M.

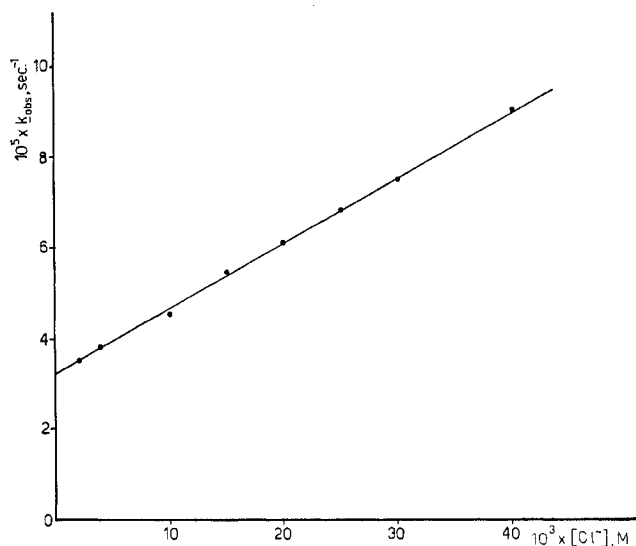
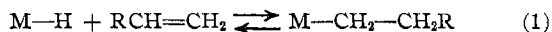


Figure 1.—Dependence of the  $k_{\text{obsd}}$  values on the chloride concentration for the reaction of  $trans\text{-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$  in ethanol at 30°; acid concentration  $2 \times 10^{-2}$  M; olefin concentration  $20 \times 10^{-2}$  M.

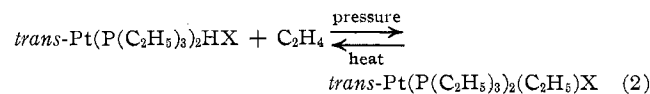
This may be due to an unfavored nucleophilic attack on the central metal by the incoming olefins, thereby preventing the starting complex from acting as a template for hydrogen transfer to the olefin. In order to elucidate the possible reaction mechanism for these processes, we will examine some of the findings reported in the recent literature concerning the properties of the olefin-metal hydride systems.

Hydrido-metal complexes of  $d^6$  and  $d^8$  configurations have been reported to undergo olefin insertion across the metal-hydrogen bond to give alkyl derivatives



The most relevant examples are the reversible reactions of  $\text{Rh}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}_2$ ,<sup>3</sup>  $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$ ,<sup>4,5</sup> and  $\text{Co}(\text{CO})_4\text{H}$ <sup>6</sup> with olefins. Equilibrium 1 is assumed as the basic mechanism of the homogeneous catalytic isomerization<sup>7-9</sup> and hydrogenation<sup>10-12</sup> of unsaturated hydrocarbons and in this regard it is of great current interest.

Ethylene is known to react reversibly with platinum-(II) hydrides



The hydrogen atom from both the methyl and the methylene group is believed to become the hydrido ligand, as indicated by H-D exchange experiments with deuterating agents.<sup>2</sup>

Equilibrium 2 lies far over to the left and depends upon the nature of both the olefin and the group *trans* to the hydride; under forcing conditions only does the reaction go to completion. As an example, at 95° (80 atm) a 25% conversion of the hydride into ethyl complex was achieved and the reverse reaction occurred when the ethyl derivative was heated to 180°.<sup>2</sup> Under such conditions, however, the olefin may isomerize through labile secondary alkyl derivatives, as found in the isomerization of 1-hexene to 2-hexene with  $trans\text{-Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$  at 170°.<sup>13</sup>

The tendency of  $\pi$ -bonded  $\text{Pt}^{\text{II}}$  complexes to convert into  $\sigma$ -bonded derivatives is common to the  $\pi$ -allyl systems. Thus,  $\text{Pt}^{\text{II}}$   $\pi$ -allyl complexes of the type  $[\text{Pt}(\text{PR}_3)_2(\text{allyl})]^+\text{Cl}^-$  give rise to a wide variety of reactions, among the most relevant of which is the formation of saturated and unsaturated hydrocarbons by the action of hydrogen and hydrogen chloride. Sulfur dioxide and carbon dioxide afford insertion products. All of these reactions point to the presence of the coordinatively unsaturated platinum- $\sigma$ -allyl complex  $\text{PtCH}_2\text{-CH}=\text{CH}_2$ , at very low concentration, which is held responsible for the high reactivity of these complexes.<sup>14</sup> The tendency to form a highly reactive  $\sigma$  intermediate resembles the ease of formation of platinum(II)-alkyl complex from the system olefin-metal hydride. In the light of these considerations, the most probable mechanism can be outlined as shown in Figure 2. This mechanism involves a fast preequilibrium step between the hydrido complex and the olefin leading to olefin insertion across the Pt-H bond. This would be followed by cleavage of the resulting  $\text{Pt}^{\text{II}}$ -alkyl complex by hydrochloric acid. The attack on the Pt-C  $\sigma$ -bonded complex by HCl should proceed through oxidative addition

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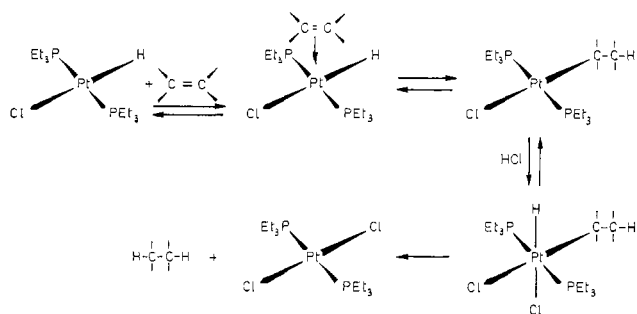


Figure 2.—Proposed reaction mechanism.

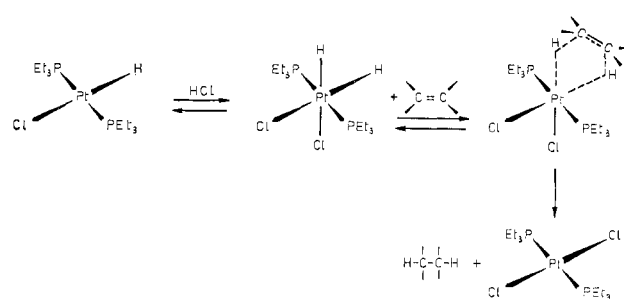


Figure 3.—Alternative pathway.

giving an unstable six-coordinate  $\text{Pt}^{\text{IV}}$  intermediate. From this species the saturated hydrocarbon would eventually split off.<sup>1</sup>

Many  $d^8$  complexes are catalysts for the homogeneous hydrogenation of unsaturated hydrocarbons under mild conditions. Among these the most effective are  $\text{Rh}^{\text{I}}$ ,<sup>3,15-17</sup>  $\text{Ir}^{\text{I}}$ ,<sup>18-20</sup> and  $\text{Pt}^{\text{II}}$ <sup>10-12,21-24</sup> complexes. It is currently believed that such catalytic activity involves the activation of molecular hydrogen leading to hydrido species which are coordinatively unsaturated and are therefore capable of interacting with the olefin, thereby facilitating the hydrogenation. The metal complex functions as a template in which the coordinated molecular hydrogen and the olefin give rise to a reactive transient intermediate which decays through an intramolecular interaction. In accord with this theory,  $d^8$  complexes which form stable hydrides, such as supposedly  $\text{Ir}(\text{P}(\text{C}_6\text{H}_5)_3)_3\text{Cl}$ ,<sup>19</sup> and/or coordinatively saturated hydrides, such as the stable platinum-hydrido complexes, are not good catalysts for hydrogenation.<sup>25</sup> The relatively high stability of platinum hydrides together with their saturated coordination makes such a reaction mechanism as sketched in Figure 3 unlikely, although in agreement with experimental data.

We are therefore inclined to believe that the mechanism which is operative in these olefin reduction processes is that represented in Figure 2. Consistently, the dihydride complex  $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{H}_2\text{Cl}_2$  prepared independently<sup>4</sup> was found to be ineffective toward olefin hydrogenation, when present as a precipitate from an ether solution. Strong evidence for the inability of the coordinatively saturated dihydride to promote olefin hydrogenation lies in the fact that 1-hexene is not hydrogenated by a dichloroethane solution of the dihydride, which is formed instantly by the action of hydrogen chloride on *trans*- $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$  and is stable

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(23) G. C. Bond and M. Hellier, *Chem. Ind. (London)*, 35 (1965).

(24) G. C. Bond and M. Hellier, *J. Catalysis*, **7**, 217 (1967).

(25) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

for a while. On the other hand, in the homogeneous hydrogenation of olefins catalyzed by Vaska's compound, the hydride  $\text{H}_2\text{Ir}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{CO})\text{Cl}$  is not directly involved in the hydrogenation, whereas the coordinatively unsaturated  $\text{H}_2\text{Ir}(\text{P}(\text{C}_6\text{H}_5)_3)(\text{CO})\text{Cl}$ <sup>26</sup> is. A similar mechanism to that which we proposed (eq 1) has been suggested for the *cis* hydrogenation of diphenylacetylene by means of an iridium(III) hydride and  $\text{HCl}$ .<sup>27</sup> Thus, the stable intermediate  $[\text{C}_6\text{H}_5\text{CH}=\text{C}-\text{C}_6\text{H}_5\text{IrCl}_2((\text{CH}_3)_2\text{SO})_3]$  was obtained by the reaction of hydridodichlorotris(dimethyl sulfoxide)iridium(III) with diphenylacetylene in propan-2-ol. Treatment of this metal-vinyl intermediate with a boiling methanolic solution of hydrochloric acid yielded *cis*-stilbene and  $\text{IrCl}_3((\text{CH}_3)_2\text{SO})_3$ .

### Experimental Section

**Materials.**—*trans*- $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$  was prepared by reduction of the *cis*-dichloro complex with hydrazine in water according to the procedure reported in the literature.<sup>4</sup> Cyclohexene, 1-hexene, 1-octene, 2-methyl-2-butene, acrylonitrile, and *trans*-dichloroethylene were pure commercial products and were used without further purification, after gas chromatographic analytical control.

**Reactions.**—The course of the reactions was monitored by means of Beckman DK-2A uv and Perkin-Elmer 621 ir spectrophotometers. In the experiment described below an Aerograph 1520 gas chromatograph was used. It was equipped with an SE 30 silicon gum rubber column maintained at 55°, the detector being at 310° and the injector at 150°. Helium was the carrier with a rate flow of 30 ml/min.

All of the reactions were carried out in ethanol at room temperature in the presence of hydrochloric acid. In a typical run, to a solution of 0.75 g of *trans*- $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{HCl}$  in 5 ml of ethanol were added 0.1 ml of hexene-1 and 0.1 ml of 2 *N* aqueous hydrochloric acid. The solution was kept in the dark at room temperature for 2 days and then the solvent was distilled off at low temperature *in vacuo*. In the distillate, hexane was identified as the main product of the reaction by means of gas chromatography. No hexene-2 has been found in the final mixture. The residue was recrystallized and identified as the dichloroplatinum(II) complex by comparing its ir spectrum as Nujol mull and its uv spectrum in methanol with the spectra<sup>28</sup> of a pure sample independently prepared. Analogous methods have been used and similar results have been achieved for the other (nonactivated) olefins. Contrarily, acrylonitrile and *trans*-dichloroethylene do not undergo any reaction under our experimental conditions.

**Attempts to Hydrogenate by Means of a Platinum Dihydride.**—The dihydride  $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{H}_2\text{Cl}_2$  was prepared following the method of Chatt and Shaw.<sup>4</sup> 1-Hexene was added to an ether suspension of the complex at room temperature with stirring.

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Even after several hours no evidence of formation of hexane was obtained.

By reaction of hydrogen chloride with *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>HCl in dichloroethane the formation of the dihydride in the solution was monitored by following the appearance of an infrared band at 2252 cm<sup>-1</sup> assigned to  $\nu(\text{Pt-H})$  [ $\nu(\text{Pt-H})$  in Nujol at 2254 cm<sup>-1</sup>]. Reduction of 1-hexene to hexane did not occur in dichloroethane.

**Kinetics.**—Fresh 99.5% ethanol solutions of Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>HCl only and 1-hexene containing mineral acid HA (HCl or HClO<sub>4</sub>) were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in a 1-cm quartz cell placed in a thermostated (30°) cell compart-

ment of a Beckman DK-2A recording spectrophotometer. The reaction was followed by scanning the spectra in the ultraviolet region from time to time. All runs were carried out under pseudo-first-order conditions by changing alternatively the concentration of olefin, acid, and chloride ion, the initial concentration of complex being kept constant. The dependence of the pseudo-first-order rate constants  $k_{\text{obsd}}$  (sec<sup>-1</sup>) on the concentrations of Cl<sup>-</sup>, H<sup>+</sup>, and olefin was investigated. The  $k_{\text{obsd}}$  values were determined as usual from the slopes of the plots of  $\log(A_{\infty} - A_t)$  vs. time.

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## Kinetic Studies on the 1:1 Complex of Iron(III) and Chromate Ions in Perchloric Acid Solution<sup>1a</sup>

BY JAMES H. ESPENSON<sup>1b</sup> AND SUSAN R. HELZER<sup>1c</sup>

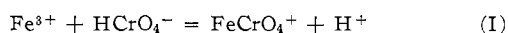
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Rate studies have been carried out on the complex formation reaction of Fe<sup>3+</sup> and HCrO<sub>4</sub><sup>-</sup>. The rate expression is  $d[\text{FeCrO}_4^+]/dt = k_f[\text{Fe}^{3+}][\text{HCrO}_4^-][\text{H}^+]^{-1} - k_a[\text{FeCrO}_4^+]$  with  $k_f = 35.0 \pm 1.3 \text{ sec}^{-1}$  and  $k_a = 15.1 \pm 1.3 \text{ sec}^{-1}$  at 25.0° and 1.00 M ionic strength (LiClO<sub>4</sub>). The stability quotient of FeCrO<sub>4</sub><sup>+</sup> obtained from the rate studies was confirmed by independent spectrophotometric measurements. The proposed mechanism involves substitution of HCrO<sub>4</sub><sup>-</sup> on FeOH<sup>2+</sup>, in accord with other iron(III) substitution reactions.

### Introduction

Complexes of CrO<sub>4</sub><sup>2-</sup> with metal ions have not been studied extensively. King and Neptune<sup>2</sup> found the intense light absorption in solutions of Cr(III) and Cr(VI) was due to the complex CrCrO<sub>4</sub><sup>+</sup> whose stability, however, was too small to evaluate. Tong and King<sup>3</sup> have found complex formation between Ce(IV) and CrO<sub>4</sub><sup>2-</sup> and Sullivan and French<sup>4</sup> studied the association of Co(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)<sup>3+</sup> and CrO<sub>4</sub><sup>2-</sup>, concluding that both slowly established and rapid equilibria were important, corresponding to inner and outer complexes.

In a kinetic study of the mechanisms of oxidation of Fe<sup>2+</sup> by HCrO<sub>4</sub><sup>-</sup>, Espenson and King<sup>5</sup> noted extensive complexing of Fe<sup>3+</sup> by HCrO<sub>4</sub><sup>-</sup> according to



We have carried out a study of the forward and reverse rates of reaction I under a wide variation of concentrations of Fe<sup>3+</sup>, HCrO<sub>4</sub><sup>-</sup>, and H<sup>+</sup> at 25.0° with lithium perchlorate added to maintain an ionic strength of 1.00 M.

### Experimental Section

**Materials.**—Hydrated iron(III) perchlorate was prepared by fuming the chloride with perchloric acid, and its solutions were

analyzed by accepted procedures.<sup>6</sup> Potassium dichromate solutions were prepared from the reagent grade solid. Lithium carbonate was used to prepare the perchlorate which was recrystallized three times. Reagent grade perchloric acid was used without further purification. All solutions were made up with conductivity water.

**Procedures.**—Spectrophotometric measurements were carried out using a Cary Model 14 recording spectrophotometer in which the sample temperature was maintained at 25.0 ± 0.2° by circulating water.

The rate studies were carried out using a spectrophotometric stopped-flow apparatus<sup>6</sup> based on the design of Dulz and Sutin.<sup>7</sup> The wavelength chosen was often 380 nm,  $\lambda_{\text{max}}$  for FeCrO<sub>4</sub><sup>+</sup>, but frequently studies were carried out at longer wavelengths to limit the total absorbance change to 0.1.<sup>6</sup>

### Results

**Rate Experiments.**—Perchloric acid was in considerable excess over the changes in concentration of the other substances, so that its concentration remained effectively constant. The rate can be represented by

$$d[\text{FeCrO}_4^+]/dt = k_f'[\text{Fe}^{3+}][\text{HCrO}_4^-] - k_a'[\text{FeCrO}_4^+] \quad (1)$$

where  $k_f'$  and  $k_a'$  represent rate constants at any particular [H<sup>+</sup>].

In all experiments the iron(III) concentration was in considerable excess over chromium(VI) so that the integrated rate expression is that given by eq 2, with concentrations replaced by absorbances ( $D$ ). The

$$-d \ln(D_{\infty} - D)/dt = k_{\text{app}} = k_a' + k_f'[\text{Fe}^{3+}] \quad (2)$$

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2459. (b) Fellow of the Alfred P. Sloan Foundation 1968–1970. (c) Based on the M.S. thesis of S. R. H., Iowa State University, Aug 1968.

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