ing step. Based on the published data no distinction can be drawn between the two proposed formulations of the reactive dinitrosyls, and it is impossible to say whether dinitrogen dioxide is a ligand in a stable intermediate, a transition state in the conversion of two-coordinated nitrosyls into a hyponitrite type structure, or simply nonexistent.

Moser[24] has recently studied the thermal decomposition of a number of dinitrosyls to yield N_2, N_2O, and NO. Product selectivity (N_2 vs. N_2O) is found to be great in several of these cases, as for instance with $RuCl(NO^+)(NO^-)L_2^+$ [25] which shows a quantitative yield of molecular nitrogen.[24] The importance of the cis dinitrosyl structure is underscored by these results, and Moser's studies start to define the steric and electronic factors which should be useful in future catalyst design.

Finally, the slow catalytic disproportionation of NO by $[RhCl_2(NO)_2]^-$ which we find following reaction 6 appears to be closely related to the observations of Stanko and coworkers.[10] Indeed, GC analysis of the gas mixture reveals that reaction of ethanolic HCl solutions of $[RhCl_2(CO)_2]^-$ with nitric oxide results in consumption of 22 mol of NO per mole of rhodium, with production of 2 mol of CO_2 and 6 mol of N_2O. Thus, if initial stoichiometric conversion according to eq 6 occurs, the mole ratio of NO to N_2O is consistent with slow catalysis of reaction 10. The dinitrosyl complex $[RhCl_2(NO)_2]^-$ differs from the reactive species proposed by Stanko in the oxidation state, but the same mechanism could be operative.

$$4NO + 2CH_3CH_2OH \rightarrow N_2O + 2CH_3CH_2ONO + H_2O \quad (10)$$

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Catalysis in Oxidation Reactions. II. The Oxalic Acid Catalyzed Oxidation of Iodide[1]

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Abstract: Oxalic acid acts as a very effective catalyst for the chromic acid oxidation of iodide. At low concentrations, the reaction is first order in oxalic acid, iodide, chromic acid, and hydrogen ions, but becomes zero order in iodide at high iodide concentrations. The proposed mechanism consists of the formation of a termolecular complex $(CO_2)_2CrIO_2^-$ formed from oxalic acid, chromic acid, and an iodide ion followed by its decomposition into an iodine atom and a chromium(V)-oxalic acid complex, $(CO_2)_2CrO_2^-$. It is assumed that the catalytic activity of oxalic acid is due to its ability to stabilize chromium(V). At high iodide concentrations, the formation of the oxalatochromate(VI), $HO_2CCO_2CrO_3^-$, from oxalic acid and $HCrO_4^-$ becomes the rate limiting step of the reaction. The rate of this reaction is about 10^4 higher than previously reported. Indirect kinetic evidence for the formation of the iodochromate ion, $ICrO_3^-$, has also been obtained.

Our observation that oxalic acid[2,3] and hydroxy acids[4-6] have a dramatic accelerating effect on the chromic acid oxidation of alcohols suggested that important new insight into the nature of oxidation processes could be obtained by investigating the effect of oxalic and of substituted carboxylic acid on other oxidation reactions. In this paper we wish to report the results of our study of the effect of oxalic acid on what is certainly the most common of all chromic acid oxidations, the oxidation of iodide ion. Although analytical chemists have been aware for some time[7,8] that the presence

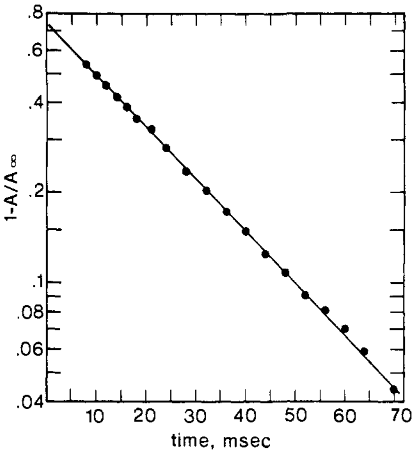


Figure 1. First-order plot for the oxalic acid catalyzed iodide oxidation. Conditions: 0.0234 M I^-, 0.0050 M $(CO_2H)_2$, 0.600 M H^+; μ = 1.17 M ($NaNO_3$).

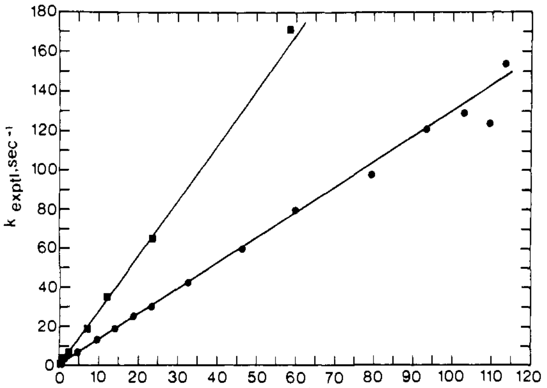


Figure 2. Dependence of oxidation rates on the concentration of oxalic acid. Conditions: (■) 0.10 M H^+, 0.050 M I^-, μ = 0.250 M; (●) 0, 80 M H^+, 0.0030 M I^-, μ = 1.17 M.

of oxalic acid accelerates the reaction between chromic acid and iodide and leads to more consistent and sharper end points in iodometric titrations of chromic acid, this observation received no attention as far as the mechanism of the process is concerned.

Experimental Section

Reagents. All reagents used were AR grade except for sodium hydrogen oxalate (Pflaltz and Bauer) which was found to contain an excess of 6.7 ± 0.1% oxalic acid. This amount of excess acid was taken into consideration when solutions were prepared. All reagents were dried and kept in a desiccator before use.

Kinetics. The reactions were monitored by following absorbance changes of the solutions at 353 nm. At this wavelength the molar absorptivity of $HCrO_4^-$ is 1560 M^{-1} cm^{-1} and that of I_3^- is 26 400 M^{-1} cm^{-1}. Measurements were performed either in an Aminco-Morrow stopped flow apparatus with a HETO type 623 constant temperature circulator or a Cary 15 spectrophotometer with a Lauda K2/R constant temperature circulator, depending on the speed of the reaction. All reactions were run at 25 °C. Good first-order plots over three half-lives were obtained (Figure 1).

Special precautions had to be implemented because it was found that not only did oxalic acid catalyze the Cr(VI)-I^- reaction but also what is presumed to be the O_2-I^- or photochemical reaction. It was determined that neither O_2 nor I_2 had any measurable effect on reaction rates or yields; however, because of the low Cr(VI) concentrations used (3×10^{-5} *M*), I_3^- formed by air oxidation did have a large effect on the initial and final absorbances measured.[9]

The following procedure was employed to minimize this problem. First, only freshly prepared solutions were used. Second, water used in the preparation of solutions was boiled and then cooled while a stream of prepurified nitrogen was bubbled through it. Third, the reactions were started by mixing two separate solutions of which one contained potassium iodide, sodium hydrogen oxalate, and/or sodium oxalate; the other solution contained potassium dichromate and nitric acid.[10] Further, iodide solutions were stored in the dark until they were used. In this way, initial amounts of both O_2 and I_2 were kept to an acceptable level. Blanks were always run with no Cr(VI) present; although air oxidation still took place to a measurable extent, it was slow enough to give minimal interference.

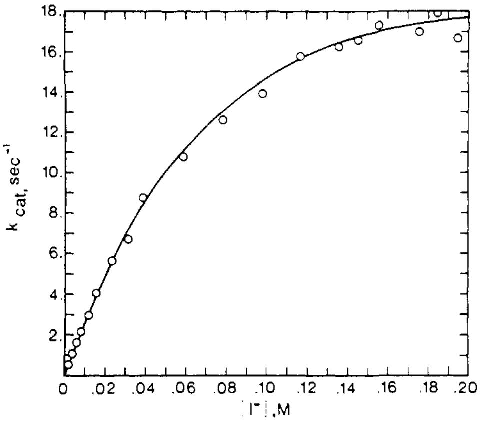


Figure 3. Dependence of oxidation rate on iodide concentration: H^+ = 0.30 M, $(CO_2H)_2$ = 0.002 M, μ = 0.50 M.

The amounts of I_3^- formed in the oxidation were determined spectrophotometrically from $A_\infty - A_0$ readings for all runs and agreed within 5% with the theoretical yield based on the stoichiometry shown in eq 1 (vide infra).

Nitric acid was used as a hydrogen ion source and sodium nitrate was used to keep ionic strength constant. It was determined that using perchloric instead of nitric acid had no effect on either the yields of I_3^- or on oxidation rates. All reactions were thermostated previously to and during runs at 25 °C.

Reactions were initiated by mixing a solution containing iodide and oxalate with one containing Cr(VI) and nitric acid. It was determined that for a reaction mixture (0.005 M in hydrogen ions, 0.061 M in total oxalate, and 0.005 M in iodide) it made no difference whether the reaction was initiated by mixing preequilibrated solutions (a) ($Cr^{VI} + I^- + H^+$) with ($(CO_2H)_2 + H^+$), (b) ($Cr^{VI} + (CO_2H)_2 + H^+$) with ($I^- + H^+$), or (c) ($Cr^{VI} + H^+$) with ($(CO_2H)_2 + I^- + H^+$). The rates were identical in all three runs.

Results and Discussion

Stoichiometry. In the whole range of reaction conditions used in this study, up to the highest concentrations of oxalic acid (0.116 M) the reaction followed the usual stoichiometry (reaction 1).

$$2Cr^{VI} + 6I^- \rightarrow 2Cr^{III} + 3I_2 \qquad (1)$$

Oxalic acid thus acts as a *catalyst* in the chromic acid oxidation of iodide ion. Its role in this reaction is quite different from that reported previously for the oxidation of alcohols where both the alcohol and oxalic acid are oxidized in a stoichiometric ratio in a cooxidation reaction.[2,3]

Kinetics. The oxidation rate is proportional to the concentration of oxalic acid over a wide range of concentrations (Figure 2). The catalysis is particularly effective at lower acidities; e.g., in 0.01 M nitric acid iodide is oxidized about 10^4 times faster in the presence of 0.0234 M oxalic acid than in its absence.

Figure 3 shows the dependence of the oxidation rate on the concentration of iodide ions. At low concentrations the reaction is clearly first order in iodide, but changes to zero order at high concentrations of iodide. At low acid concentrations, good straight-line plots are obtained when the reciprocal of the pseudo-first-order rate constant for the catalyzed reaction, k_{cat}, is plotted against $1/[I^-]$ (Figure 4).[11]

Several mechanisms consistent with this behavior can be proposed. The most plausible ones are given in Schemes I-III.

Scheme I assumes the formation of $ICrO_3^-$ is responsible for the change from first to zero order in iodide.

Scheme I

$$HCrO_4^- + I^- + H^+ \overset{K_2}{\rightleftharpoons} ICrO_3^- \tag{2}$$

$$ICrO_3^- + (CO_2H)_2 \xrightarrow{k_3} \text{products} \tag{3}$$

This mechanism corresponds to the rate law

$$v = \frac{d[I_3^-]}{dt} = -\frac{3}{2}\frac{d[Cr(VI)]}{dt} =$$
$$k_{cat}[Cr(VI)] = k_3[ICrO_3^-][(CO_2H)_2] = k_3K_2[HCrO_4^-][I^-][(CO_2H)_2][H^+] \tag{4}$$

Chromium(VI), according to this mechanism, is present both as $HCrO_4^-$ and as $ICrO_3^-$,

$$[Cr(VI)] = [HCrO_4] + [ICrO_3^-] = [HCrO_4^-]\,(1 + K_2[I^-][H^+]) \tag{5}$$

Therefore,

$$k_{cat} = \frac{k_3K_2[I^-][(CO_2H)_2][H^+]}{1 + K_2[I^-][H^+]} \tag{6}$$

$$\frac{1}{k_{cat}} = \frac{1}{k_3K_2[(CO_2H)_2][H^+]}\frac{1}{[I^-]} + \frac{1}{k_3[(CO_2H)]} \tag{7}$$

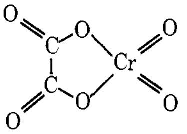
If we define a constant A = 1/intercept and B = intercept/slope, where the values of the intercepts and slopes are obtained from plots of $1/k_{cat}$ vs. $1/[I^-]$, then

$$A = k_3[(CO_2H)_2]; \quad B = K_2[H^+] \tag{8}$$

In Scheme II we assume that chromic acid reacts with oxalic acid and that iodide reacts with the resulting complex.

Scheme II

$$HCrO_4^- + (CO_2H)_2 + H^+ \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}}$$



(9)

$$(CO_2)_2CrO_2 + I^- \xrightarrow{k_{10}} \text{products} \tag{10}$$

The formation of chromyl oxalate is known from our previous work;[12] the equilibrium constant $k_9/k_{-9} = 7.5\ M^{-2}$ at 25° (μ = 0.63 M). The rate law derived from Scheme II is

$$v = k_{cat}[Cr(VI)] = \frac{k_9k_{10}[HCrO_4^-][(CO_2H)_2][I^-][H^+]}{k_{-9} + k_{10}[I^-]} \tag{11}$$

Assuming for the moment that all chromium(VI) is present in the form of the acid chromate ion, i.e., that $[Cr(VI)] = [HCrO_4^-]$, then

$$\frac{1}{k_{cat}} = \frac{k_{-9}}{k_9k_{10}[(CO_2H)_2][H^+]}\frac{1}{[I^-]} + \frac{1}{k_9[(CO_2H)_2][H^+]} \tag{12}$$

$$A = k_9[(CO_2H)_2][H^+]; \quad B = k_{10}/k_{-9} \tag{13}$$

Scheme III is similar to Scheme II, except that it is assumed that the reaction of oxalic acid with the monochromate anion leads in the first step to the formation of oxalylchromate, $HO_2CCO_2CrO_3^-$, rather than to the neutral chromyl oxalate $(CO_2)_2CrO_2$.

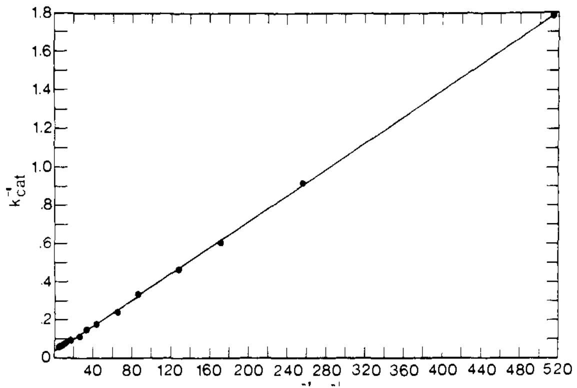


Figure 4. Inverse rate vs. concentration plot for 0.30 M H^+ solutions. Same data as in Figure 3.

Scheme III

$$HCrO_4^- + (CO_2H)_2 \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} HO_2CCO_2CrO_3^- \tag{14}$$

$$HO_2CCO_2CrO_3^- + I^- + H^+ \xrightarrow{k_{15}} \text{products} \tag{15}$$

$$k_{cat} = \frac{k_{14}k_{15}[(CO_2H)_2][I^-][H^+]}{k_{-14} + k_{15}[I^-][H^+]} \tag{16}$$

$$\frac{1}{k_{cat}} = \frac{k_{-14}}{k_{14}k_{15}[(CO_2H)_2][H^+]}\frac{1}{[I^-]} + \frac{1}{k_{14}[(CO_2H)_2]} \tag{17}$$

$$A = k_{14}[(CO_2H)_2]; \quad B = k_{15}[H^+]/k_{-14} \tag{18}$$

Both Schemes II and III assume a change in rate limiting step from oxidation to the formation of the intermediate chromic acid-oxalic acid complex $(CO_2)_2CrO_2$ or $HO_2CCO_2CrO_3^-$, respectively, whereas Scheme I assumes a complete conversion of chromium(VI) into the reactive intermediate $ICrO_3^-$ at high concentrations of iodide ions.

All three mechanisms result in the same type of rate law which is first order in $HCrO_4^-$, $(CO_2H)_2$, I^-, and H^+ at low iodide concentrations and will become zero order in iodide at high iodide concentrations; all three will give straight line reciprocal plots from which the constants A and B can be determined. Scheme II requires that the constant A is proportional to the concentration of hydrogen ions and that B is acidity independent whereas Schemes I and III both predict an acidity independent A and a B which will be proportioned to the concentration of hydrogen ions.

Table I summarizes the experimental data obtained in eight series of kinetic runs at different acidities and with different concentrations of oxalic acid. The results show unambiguously that B rather than A is proportional to the hydrogen ion concentration. Scheme II thus can be eliminated from further consideration.

It is much more difficult to distinguish between Schemes I and III. The postulated formation of the iodochromate ion $ICrO_3^-$ is quite consistent with the behavior of other halide ions

$$HCrO_4^- + X^- + H^+ \overset{K}{\rightleftharpoons} XCrO_3^- \tag{19}$$

The equilibrium constant for[13] $X^- = Cl^-$ is $K = 11.1\ M^{-2}$; for[14] $X^- = Br^-$, $K = 3.3\ M^{-2}$. Thus the value of $K = K'/[H^+] = 39.1\ M^{-2}$ is of approximately the correct order of magnitude, but appears too high. Particularly the trend I^-

Table I. Equilibrium and Rate Constants from Reciprocal Plots of k_{cat} vs. $[I^-]$

$[H^+]$,[a] M	$10^3[(CO_2H)_2]$,[b] M	$10^3[I^-]$, M (no. of concentrations)	Ionic strength, M	A[c]	B[d]	$10^{-4}[A/[(CO_2H)_2]] = k_{14}$	$B/[H^+] = k_{15}/k_{-14}$
0.030	0.50	22-217 (10)	0.250	5.88	1.12	1.18	37.3
0.030	10.00	18-180 (10)	0.250	118	1.24	1.18	41.3
0.100	3.00	1.4-140 (15)	0.250	38.8	3.75	1.29	37.5
0.100	15.00	0.72-144 (16)	0.250	192	4.30	1.28	43.0
0.100	2.00	2.0-394 (13)	0.500	25.0	4.0	1.25	41.0
0.300	2.00	2.0-195 (19)	0.500	25.3	11.7	1.27	39.0
0.300	5.00	2.2-559 (23)	1.17	58.8	11.3	1.18	37.7
0.600	5.00	2.2-559 (23)	1.17	66.7	21.8	1.33	36.3
				Average		1.24×10^4	39.1

[a] Calculated from the amounts of HNO_3, oxalic acid, and/or its sodium salts used, and from the dissociation constant of oxalic acid, $K_a = 0.059$ ("Handbook of Chemistry and Physics", 51st ed, The Chemical Rubber Co., Cleveland, Ohio, 1970). [b] Free oxalic acid, calculated from $[(CO_2H)_2] = [\text{oxalic acid}]_{total}[H^+]/(K_a + [H^+])$. [c] A = 1/intercept. [d] B = intercept/slope.

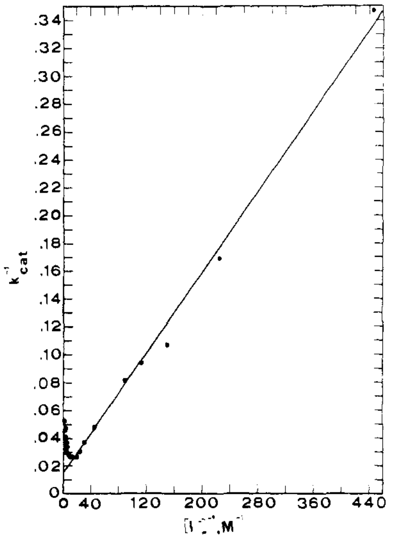


Figure 5. Inverse rate vs. concentration plot for 0.60 M H^+ solutions. Oxalic acid = 5×10^{-3} M, μ = 1.17 M.

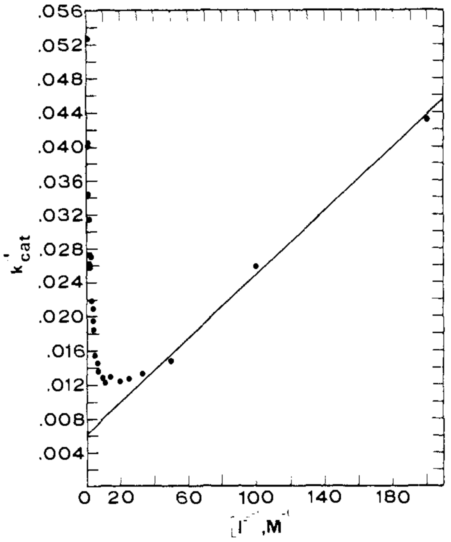


Figure 6. Inverse rate vs. concentration plot for 1.0 M HNO_3 solutions. Oxalic acid = 0.01 M, μ = 2.0 M.

$> Cl^- > Br^-$ is quite unexpected. An even more disturbing feature was that none of the numerous investigations of the chromic acid oxidation of iodide[15-19] revealed any of the features (change in the order of the reaction) which one would predict if reaction 2 of Scheme I actually took place and had a large equilibrium constant. To reconcile the assumption of the formation of $ICrO_3^-$ with a large formation constant with lack of any change in the order in iodide ions in the uncatalyzed chromic acid oxidation of iodide, one would have to assume a fortuitous cancellation of two opposing effects. To introduce the assumption of the formation of $ICrO_3^-$ with a formation constant $K = 39.1$ M^2 would require a very complex mechanism for the uncatalyzed chromic acid oxidation of iodide. Moreover, our attempts to observe an analogous change from first to zero order in iodide at the same iodide concentration with another catalyst, tartaric acid, was unsuccessful. Thus, although we cannot rule mechanism I out rigorously, we consider it quite unlikely.

The mechanism given in Scheme III implies that the formation of the complex between oxalic acid and the monochromate anion (eq 14) becomes the rate limiting step at high concentrations of iodide. From Table I and eq 18 it can be seen that the second-order rate constant for this step would be 1.24×10^4 M^{-1} s^{-1}. This rate constant in itself is quite plausible. It is of a similar order of magnitude as other reactions of $HCrO_4^-$ with acids.[20] It is also entirely reasonable to assume that the rate limiting step in the formation of the cyclic chromyl oxalate (eq 9) is the formation of the acyclic anion (eq 14). For a long time, however, we were reluctant to accept this conclusion and, consequently, mechanism III because this rate constant is about 10^4 times higher than that previously reported for the same reaction,[21] albeit under somewhat different conditions.[22]

However, we recently found that the oxalic acid catalyzed chromic acid oxidation of ferroin,[23] for which a mechanism of type I is most improbable, also exceeds the previously reported limiting rate for the formation of the chromic acid-oxalic acid complex (reaction 14) by several orders of magnitude. We therefore must conclude that the previously determined rate constant for reaction 14 must be in error[24] and conclude that the oxalic acid catalysis of iodide oxidation does proceed by mechanism III.

While good straight lines for $1/k_{exptl}$ vs. $1/[I^-]$ plots were obtained at lower acidities (Figure 4), a departure from linearity became clearly noticeable at high acidities and high iodide concentration (Figures 5 and 6). Under these conditions the reaction rates are lower than predicted on the basis of Scheme III. We believe that these deviations are due to the conversion of a substantial portion of chromium(VI) into the iodochromate ion $ICrO_3^-$ (eq 2) under these conditions. This reaction is much more important in the uncatalyzed chromic acid oxidation of iodide ions, the investigation of which led to the determination of equilibrium constants at several concentrations of nitric acid.[25] Thus, at high acidities and iodide concentrations the formation of $ICrO_3^-$ must be taken into account and will be reflected in the rate law. From eq 5 and 16 we obtain

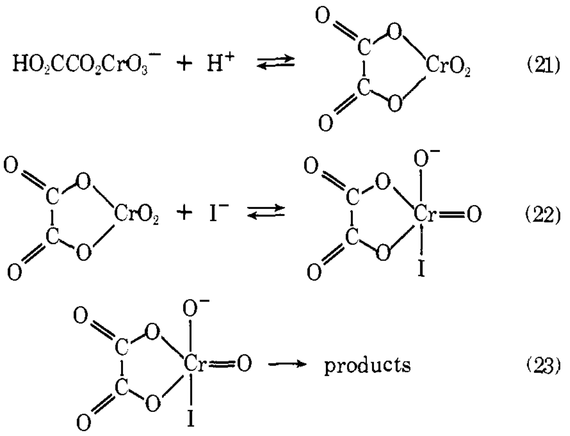
$$k_{\text{cat}} = \frac{k_{14}k_{15}[(\text{CO}_2\text{H})_2][\text{I}^-][\text{H}^+]}{(k_{-14} + k_{15}[\text{I}^-][\text{H}^+])(1 + K_2[\text{I}^-][\text{H}^+])} = \frac{k_{14}k_{15}[(\text{CO}_2\text{H})_2][\text{I}^-][\text{H}^+]}{k_{-14} + (k_{15} + k_{-14}K_2)[\text{I}^-][\text{H}^+] + k_{15}K_2[\text{I}^-]^2[\text{H}^+]^2} \tag{20}$$

Equation 20 requires that, at high acidities, the reaction rate should change from first order to zero order and finally to minus first order in iodide with increasing iodide concentration. This behavior is indeed at least approximately observed in 1 M nitric acid (Figure 7) which shows the experimental points for both the catalyzed and the uncatalyzed reaction, as well as their difference ($k_{\text{cat}} = k_{\text{exptl}} - k_{\text{uncat}}$) and the calculated curves (eq 16 and 20).[26]

Mechanism. The rate law requires that the reaction goes through a termolecular activated complex formed from iodide, chromic acid, and oxalic acid and having one negative charge (Scheme IV).

Scheme IV

$$\text{HCrO}_4^- + (\text{CO}_2\text{H})_2 \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} \text{HO}_2\text{CCO}_2\text{CrO}_3^- \tag{14}$$



At high iodide concentrations reaction 14 is the rate limiting step; at lower iodide concentrations reaction 14 becomes reversible and reaction 22 or reaction 23, the formation or the oxidative decomposition of the termolecular complex, becomes rate limiting.

In principle the decomposition of the complex can take place in three ways. It can correspond to a one-electron oxidation leading to the formation of an iodine atom and a chromium(V) intermediate

$$(\text{CO}_2)_2\text{CrIO}_2^- \rightarrow \text{I} + (\text{CO}_2)_2\text{Cr}^{\text{V}}\text{O}_2^- \tag{24}$$

to a two-electron oxidation resulting in the formation of I^+ (or IOH) and Cr(IV)

$$(\text{CO}_2)_2\text{CrIO}_2^- \rightarrow \text{I}^+ + (\text{CO}_2)_2\text{Cr}^{\text{IV}}\text{O}_2^{2-} \tag{25}$$

or to a three-electron oxidation

$$(\text{CO}_2)_2\text{CrIO}_2^- \rightarrow \text{I}^{2+} + \text{Cr(III)} \tag{26}$$

Equation 26 appears very unlikely as it would require the formation of a very unstable valence state of iodine.

It is much more difficult to chose between eq 24 and 25. Although neither of them can be rigorously excluded, we believe that there are sufficient grounds to consider the one-electron oxidation-reduction (eq 24) more likely. This reaction leads to the formation of a chromium(V) complex of oxalic acid.

While chromium(V) is an extremely unstable species in aqueous solutions and will either immediately disproportionate into chromium(VI) and chromium(III) or react with an oxidizable substrate, it becomes quite stable in the presence of oxalic acid where it presumably exists in the form of a chromium(V)-oxalic acid complex.[27] This greatly increased stability of chromium(V) relative to chromium(VI) must of course make the chromium(VI)-oxalic acid complex a much stronger one-electron oxidant than aqueous chromium(VI); the increased oxidative power provides the most plausible explanation for the ability of oxalic acid to catalyze the reaction. Additional support for this conclusion can be found in the recent observation[23] that oxalic acid also acts as a very effective catalyst in the chromic acid oxidation of ferroin for which a one-electron oxidation is very strongly indicated.

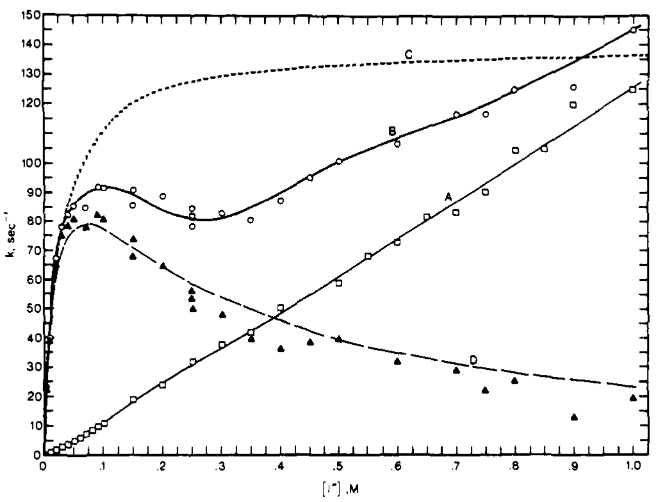


Figure 7. Dependence of rate constants on iodide concentrations in 1 M HNO_3: A, k_{uncat} (no oxalic acid); B, k_{exptl} in 0.010 M oxalic acid; C, calculated k_{cat} from eq 16 (formation of ICrO_3^- neglected); D, calculated k_{cat} for eq 20 (formation of ICrO_3^- included); points for $k_{\text{cat}} = k_{\text{exptl}} - k_{\text{uncat}}$ from curves B and A.

At this point it would be difficult to judge whether the chromium(V) complex found in reaction 24 will be reduced to chromium(III) in a two-electron oxidation or in a sequence of two one-electron steps.

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(9) Solutions that could not be used the same day as prepared had to be discarded because their initial absorbances were usually greater than 1.0. E.g., a solution of oxalic acid (0.05 M) was brought through three cycles of freezing, evacuation, thawing, and addition of prepurified nitrogen; subsequently KI (0.1 M) was added to the frozen solution under prepurified nitrogen, the mixture was evacuated once more and was then left to stand in a semidarkened room; a slight yellow tinge developed overnight. Opening the flask to the atmosphere in a lighted room and swirling the solution turned this solution a deep red within an hour's time. Sodium bioxalate accelerated the air oxidation of iodide solutions much less than oxalic acid; sodium oxalate had no affect. The rate of the air oxidation depends both on the concentration of oxalic acid and on the pH of the solution.
(10) Mono- and disodium and potassium salts of oxalic acid have limited solubilities. In order to obtain the fairly high final concentrations of oxalic acid in the reaction mixtures, we worked with a combination of sodium and potassium ions; iodide was used as the potassium salt, while oxalic acid was introduced as a mixture of sodium hydrogen oxalate and of sodium oxalate.

(11) The rate constant k_{cat} is practicably identical with the experimental rate constant k_{exptl} at low to moderate iodide concentrations. At high acidities and iodide concentrations the rate of the uncatalyzed reaction becomes large enough to make it necessary to substract it from the experimental rate: $k_{cat} = k_{exptl} - k_{uncat}$.

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(22) At pH 1.5–3.0 in the presence of 0.5 M ammonium sulfate.

(23) R. E. Hintze and J. Rocek, unpublished results.

(24) In order to test whether ammonium sulfate could in fact change the rate of reaction 14 so drastically, Dr. Hintze in this laboratory measured the rate of oxidation of iodide at pH 2.2 in the presence of 0.5 M ammonium sulfate but obtained a rate only 20% lower than that obtained in the nitric acid–sodium nitrate system. Considering the uncertainty in the equilibrium constant for $CrSO_7^{2-}$ and in the dissociation constant of oxalic acid, the rate in sulfate media is in good agreement with the rate in nitrate media.

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(26) The following values were used in the calculations: $k_{14} = 1.45 \times 10^4$ M^{-1} s^{-1}; $k_{15}/k_{-14} = 39$ M^2; $K_2 = 5.0$ M^2. The value for k_{14} is somewhat higher than the average value of 1.24×10^4 given in Table I. It was used because it gave a better fit and can be well justified in this medium of high acidity and high ionic strength ($\mu = 2.0$ M).

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Oxidative Coupling of the Phenylethynyl Group in μ-(1-3η:2-4η-*trans,trans*-1,4-Diphenylbutadiene)-bis(bis(η^5-methylcyclopentadienyl)titanium) and the Reaction of 1,4-Diphenyl-1,3-butadiene with Bis(cyclopentadienyl)titanium(II)

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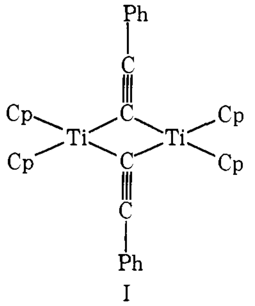
Abstract: The reaction of phenylethynylsodium, $Na(C{\equiv}CC_6H_5)$, with bis(methylcyclopentadienyl)titanium(III) chloride has been shown to result in the oxidative coupling of two phenylethynyl anions with complexation to two $(\eta^5\text{-}CH_3C_5H_4)_2Ti$ groups. The resulting complex, μ-(1-3η:2-4η-*trans,trans*-1,4-diphenylbutadiene)-bis(bis(η^5-methylcyclopentadienyl)titanium), is closely related to the uncoupled dimeric species, $[(\eta^5\text{-}CH_3C_5H_4)_2Ti{\equiv}CC_6H_5]_2$, and it is suggested that the latter is an intermediate in the coupling reaction. In view of the fact that the same molecule can be prepared by the reaction of $(C_5H_5)_2Ti^{II}$ with 1,4-diphenyl-1,3-butadiyne, the compound can be considered as a complex of two molecules of $(\eta^5\text{-}CH_3C_5H_4)_2Ti^{II}$ with 1,4-diphenylbutadiyne. The molecule, $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2C_4(C_6H_5)_2$, is located in the solid state on a crystallographic center of inversion with all of the atoms of the $(C_6H_5)_2C_4$ group and the two titanium atoms approximately coplanar. The titanium-carbon bond lengths of 2.083 (2) and 2.153 (2) Å are consistent with other titanium σ-bonded species, and the configuration about the titanium atom is the first four-membered metallocyclic geometry observed for an early transition metal organometallic compound. The hydrocarbon bond lengths are close to those expected for 1,4-diphenylbutadiene (or a reduced form of 1,4-diphenylbutadiyne). $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2C_6H_5]_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14, C_{2h}^5) with $a = 10.133$ (2), $b = 14.838$ (4), $c = 10.530$ (3) Å, $\beta = 106.97$ (1)°, $Z = 2$, $\rho_{calcd} = 1.347$, and $\rho_{exptl} = 1.38$ (3) g cm^{-3}. Full matrix least-squares refinement of 1975 x-ray diffractometer data gave $R_w = 0.037$ and $R = 0.052$.

Bis(cyclopentadienyl)titanium phenylethynyl was first prepared by Teuben and de Liefde Meijer in 1969.[1] They suggested the following two structures to be the most probable for the compound



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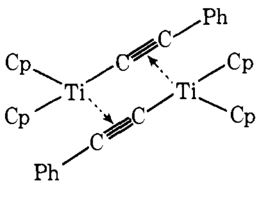

II

but preferred structure II because of the lack of a $\nu(C{\equiv}C)$ stretching band in the infrared spectrum of the compound. A dimeric structure was assumed from mass spectral evidence, but the possibility of the compound being a polymer was also suggested in view of the compounds' insolubility in both polar and nonpolar solvents.

Our interest in this material developed from earlier studies of magnetic interactions in low valent titanium organometallic systems.[2-4] A remeasurement of the magnetic susceptibility confirmed the fact that the compound is diamagnetic. A superexchange coupling through s or p carbon orbitals in structure I or a direct metal-metal interaction could lead to a large antiferromagnetic exchange interaction and the observed diamagnetism. An example of the geometry shown in configuration I for main group metals is found in $\{[N(CH_3)_3](CH_3)BeC{\equiv}CCH_3\}_2$.[5] A model for structure II has been recently reported, i.e., $[(C_6H_5)_2AlC{\equiv}CC_6H_5]_2$, in which there is a 90° Al-C-Al