

# Stopped-Flow Kinetics of the Chromium(VI) Oxidation of Malachite Green in the Presence of Oxalic Acid

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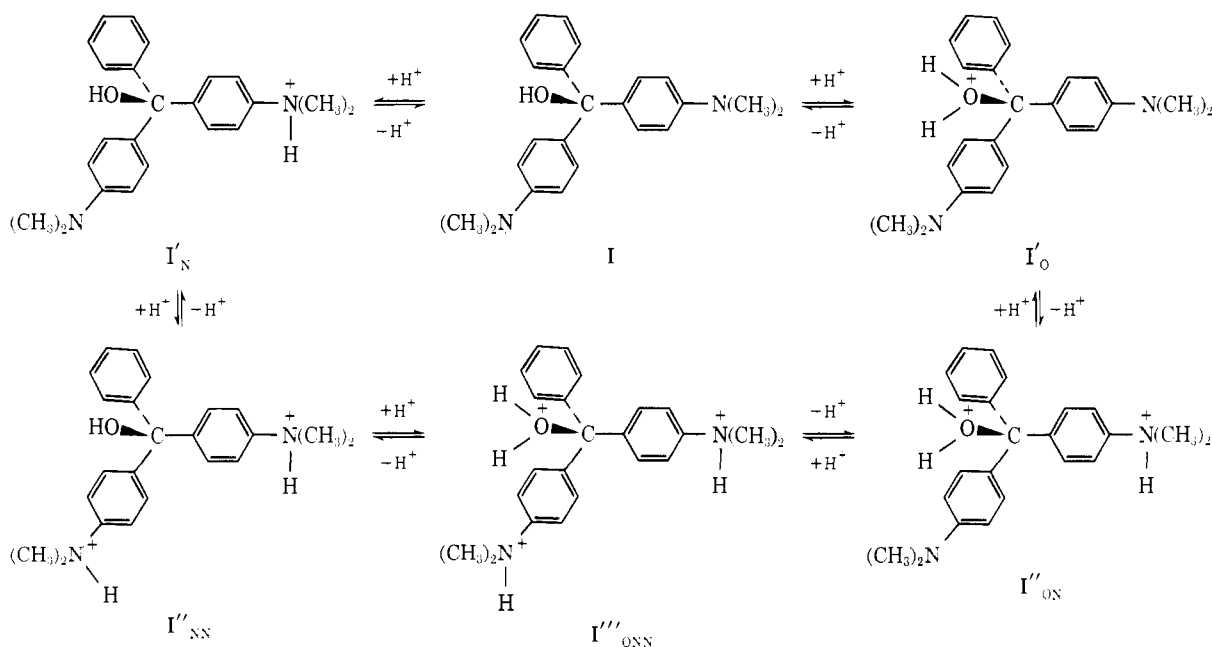
**Abstract:** The kinetics of the Cr(VI) oxidation of Malachite Green in the presence of oxalic acid have been studied spectrophotometrically by the stopped-flow method. The results are explained in terms of the reversible formation of a Cr(VI)-oxalic acid complex which oxidizes both the colorless and the colored forms of Malachite Green to benzoic acid and the diphenoquinone bis(dimethylimmonium) salt. The formation of the oxidizing complex is rate limiting for the oxidation of the colorless form, resulting in a pseudo-zeroth-order oxidation law for this substrate, whereas the attack of the oxidant becomes rate limiting for the less reactive colored form giving rise to a pseudo-first-order time dependence. The acidity effects indicate that the oxidizing species is an intermediate formed from chromate and oxalate carrying a mononegative charge. The attack of the oxidizing species on the colored form of Malachite Green is acid catalyzed. By assuming a steady-state concentration for the oxidant, the rate law for the overall reaction is derived.

An aqueous solution of "Malachite Green dye" consists of a mixture of two distinctly different chemical species.

The first species is the colorless tertiary alcohol I which shows no absorptions in the visible part of the spectrum and is commonly known as the "carbinol base" or "color base." In this species, the tetragonal carbon is covalently bonded to the hydroxyl group. Depending on the acidity of the solution, I may exist in several mono-, di-, and triprotonated forms, the structures of which are shown in Scheme I. The

range with maxima around 620 and 420 nm, respectively. The dye II is evidently at the same oxidation level as the tertiary alcohol I, since the interconversion of the two species involves only dehydration-hydration reactions. However, the valence states at the central carbon atom and consequently the molecular geometry of I and II are rather different. The well known resonance formulation of II as shown in Scheme II involves the equivalent quinoid-immonium ions, IIa'  $\leftrightarrow$  IIb', and the carbonium ion, IIc'. This unprotonated form of II is responsible for the absorption at 620 nm. The

Scheme I



notation employed in the scheme indicates the number of positive charges that have been added and the atoms (N or O) to which the protons have been added.

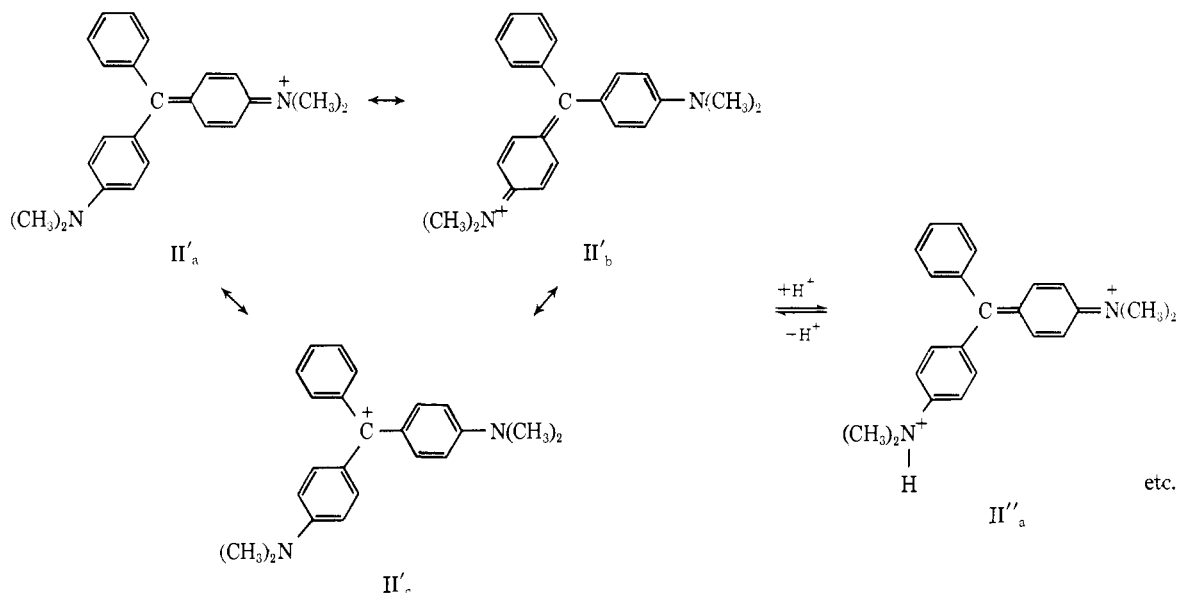
The second species, II, represents the blue-green "colored dye" and has two absorptions in the visible

range with maxima around 620 and 420 nm, respectively. The dye II is evidently at the same oxidation level as the tertiary alcohol I, since the interconversion of the two species involves only dehydration-hydration reactions.

A diprotonated form, if it is formed at all, should exist only in very highly acidic media, since the unshared electron pair of the unprotonated nitrogen in IIa'  $\leftrightarrow$  IIb' is highly delocalized and hence very weakly basic. In the presence of strong oxidants like Ce(IV),

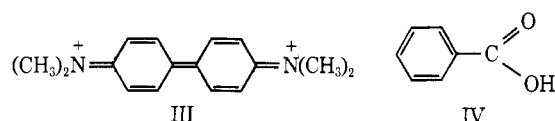
(1) (a) American Cyanamid Company; (b) State University of New York.

Scheme II



Pb(IV), or Mn(VII), the "Malachite Green dye" is known to be oxidized to the diphenoquinone bis(dimethylimmonium) salt, III, which has an absorption maximum at 460 nm, and benzoic acid, IV.<sup>2</sup> The structures of the oxidation products are depicted in Scheme III. The same oxidation products are ob-

Scheme III



tained if a Malachite Green dye solution is subjected to anodic oxidation.<sup>3</sup>

If Cr(VI) is used as the oxidant, the reaction at pH > 1 occurs only in the presence of oxalic acid. This accelerating effect of oxalic acid on the Cr(VI) oxidation of the Malachite Green system has been known for a long time.<sup>4,5</sup> The earliest report, however, concerns the oxidation of indigo, in which case the action of oxalic acid has been ascribed to the formation of a mixed anhydride of chromic and oxalic acids,  $\text{HOCrO}_2\text{-OOCOOH}$ , which is considered to be a much stronger oxidizing agent than Cr(VI) alone.<sup>6</sup> Recently, it has been reported that the well-documented Cr(VI) oxidation of 2-propanol<sup>7</sup> is likewise accelerated in the presence of oxalic acid. In this case, the cyclic form of the mixed anhydride of chromic and oxalic acids is assumed to be the oxidizing species. The strongly oxidizing properties of this species are explained by the fact that its formation facilitates the transfer of three electrons, which are required for the reduction of Cr(VI) to Cr(III), by simultaneously oxidizing part of the oxalic acid.<sup>8,9</sup> A similar three-electron oxidation has

been proposed in the case of the Cr(VI) oxidation of S(IV).<sup>10</sup>

We have quantitatively examined the effect of added oxalic acid on the Cr(VI) oxidation of Malachite Green. Moreover, we have used the Cr(VI)-oxalic acid system to study the oxidation kinetics of the different Malachite Green species, I and II. To prevent the interconversion of I and II, the kinetics of their oxidation have to be studied at a short time scale which requires the application of the stopped-flow method.

### Experimental Section

**Materials Used.** Malachite Green oxalate was a purified technical product (American Cyanamid Co.). Its purity is difficult to establish since the extinction coefficient is not only a function of pH, time, ionic strength, and concentration but also sensitive toward the way the dye has been synthesized, stored, and dried.<sup>11</sup> The material used for this study gave  $\epsilon_{618} = 8.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  in water at pH 4.0 which agrees with the highest values reported in the literature.<sup>12</sup> The oxidation product of Malachite Green, tetramethyldiphenoquinone immonium ion, was synthesized by oxidation with lead dioxide and isolated as the diperchlorate.<sup>2a</sup> The yield was 55%;  $\epsilon_{460} = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was obtained at pH 3.0 after recrystallization. All other materials used were reagent grade.

**Stopped-Flow Apparatus.** The Gibson type stopped-flow reactor consisted of a variable speed infusion-withdrawal pump (Harvard Apparatus Company) with 50-ml driving syringes and an all-Teflon mixing system with a 0.5-cm silica observation cell. The stop-flow is effected by a microswitch control on the exhaust syringe which shuts off the pump at the same time that it triggers the recording device. The optical system incorporates a Bausch and Lomb 250-mm Monochromator, IP28 photomultiplier, and a modified Aminco microphotometer. The output of the photomultiplier was recorded either by a Moseley Autograph X-Y recorder, or a Tektronix storage oscilloscope equipped with a Polaroid camera. The drive syringes, the mixing block, and the reaction cell are thermostated.

**Determination of the Stoichiometry.** The stoichiometry of the reaction was established by adding Cr(VI) in concentrations ranging from  $5 \times 10^{-4}$  to  $4 \times 10^{-3} \text{ M}$  to a solution containing  $5 \times 10^{-4} \text{ M}$  Malachite Green and 0.1 M oxalic acid at pH 3.0. After a period of 4 hr the Malachite Green concentration which remained after completion of the reaction was determined spectrophotometrically.

**Kinetic Procedures.** The reactant solutions were made up by

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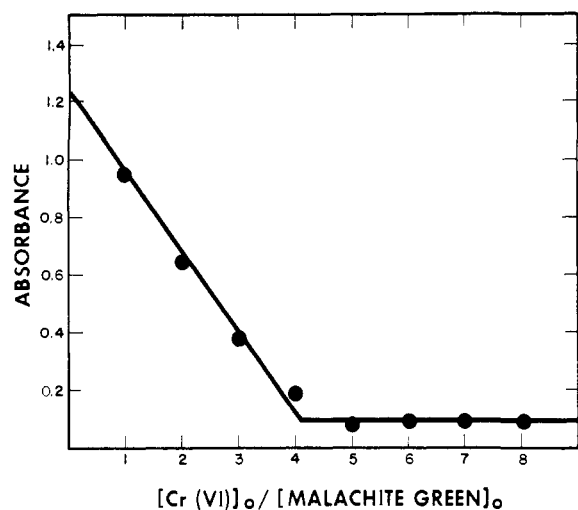


Figure 1. Determination of the oxidation stoichiometry by spectrophotometric titration of Malachite Green with Cr(VI) in the presence of excess oxalic acid.

suitable dilution of the following stock solutions:  $1.00 \times 10^{-3}$  M Malachite Green; 0.100 M potassium dichromate; 0.500 M oxalic acid; and 0.5 M potassium hydroxide. The pH of the reactant solutions was adjusted to the desired values by the addition of either potassium hydroxide or sulfuric acid.

In the experiments which required a buffering of the Cr(VI) solution, 0.2 M potassium hydrogen phthalate was added and the pH adjusted to 3.0 by the addition of concentrated hydrochloric acid.

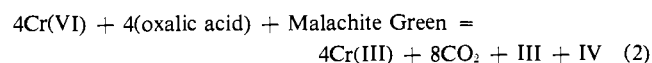
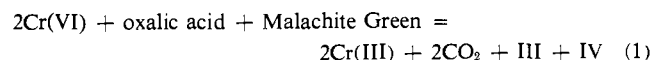
In those experiments in which the total acidity was varied, 0.5 M ammonium sulfate was added to both reactant solutions as a swamping electrolyte to eliminate the effects of changing ionic strength.

The reactions were monitored at 460 and 620 nm. The absorbance,  $A$ , at 460 nm was corrected for the contribution of Cr(VI). Each kinetic run was repeated at least three times at each wavelength. The reproducibility of the rate constants was about  $\pm 5\%$ .

## Results

The suitable acidity range to study the oxidation of the Malachite Green dye solution by spectrophotometric methods is  $1.5 < \text{pH} < 3.5$ ; at  $\text{pH} < 1.5$   $A$  (620 nm) for II' becomes too small, while at  $\text{pH} > 3.5$  the reaction product III decomposes as indicated by the slow decrease of  $A$  (460 nm) after completion of the oxidation.

The oxidation of Malachite Green to the end-products III and IV involves the transfer of a total of four electrons; therefore, the participation of more than one Cr(VI) is required. If one assumes that, by analogy to the 2-propanol system, the oxidation by Cr(VI) in the presence of oxalic acid represents a three-electron oxidation involving the cooxidation of oxalic acid,<sup>8</sup> as given in eq 1 and 2, two alternative stoichiometries are possible.



In the first case a stoichiometric ratio of  $[\text{Cr(VI)}]_0/[\text{Malachite Green}]_0 = 2$  is expected, while a stoichiometric ratio of  $[\text{Cr(VI)}]_0/[\text{Malachite Green}]_0 = 4$  should indicate that the reaction proceeds according to eq 2.

According to the results shown in Figure 1, an initial concentration ratio of  $[\text{Cr(VI)}]_0/[\text{Malachite Green}]_0 = 4$  is required to completely oxidize the Malachite

Table I. Equilibrium and Rate Constants for the Protonation and Hydration of the Different Malachite Green Species<sup>a</sup>

Equilibrium constants	
$K_1 = [\text{II}''']/[\text{II}'][\text{H}^+]$	$K_1 = 30.0 \text{ M}^{-1}$
$K_2 = [\text{I}''']/[\text{II}''']$	$K_2 = 15.1$
$K_3 = [\text{I}'][\text{H}^+]/[\text{I}''']$	$K_3 = 3.1 \times 10^{-5} \text{ M}$
$K_4 = [\text{II}''']/[\text{I}']$	$K_4 = 89.9$
Rate constants	
$k_2: \text{II}'' + \text{H}_2\text{O} \rightarrow \text{I}''$	$k_2 = 6.51 \times 10^{-3} \text{ sec}^{-1}$
$k_{-2}: \text{I}'' \rightarrow \text{II}'' + \text{H}_2\text{O}$	$k_{-2} = 4.30 \times 10^{-4} \text{ sec}^{-1}$
$k_4: \text{I}' \rightarrow \text{II}' + \text{H}_2\text{O}$	$k_4 = 2.48 \times 10^{-2} \text{ sec}^{-1}$
$k_{-4}: \text{II}' + \text{H}_2\text{O} \rightarrow \text{I}'$	$k_{-4} = 2.76 \times 10^{-4} \text{ sec}^{-1}$

<sup>a</sup> The data are taken from ref 13 and extrapolated to  $T = 30^\circ$  using the activation energies reported for Methyl Green: R. Cigén, *Acta Chem. Scand.*, **14**, 979 (1960).

Green. This indicates that for the conditions of our experiments the stoichiometry according to eq 2 is operative.

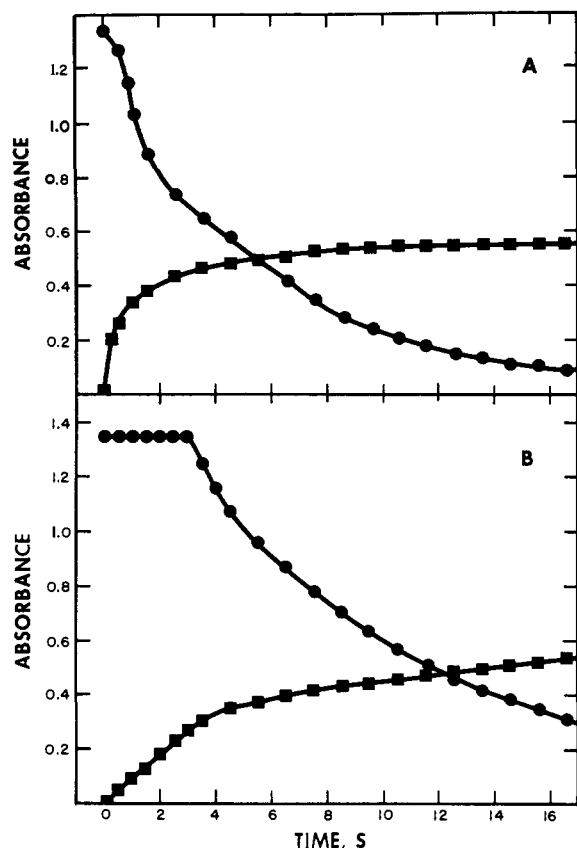
In the acidity region examined, the only species which contribute significantly to the overall concentration of the Malachite Green dye are the colorless alcohol species I' and I'' and the corresponding colored monocation II' and dication II''. The constants of the pH dependent, rapid protolytic equilibria between I' and I'' and II' and II'' respectively and for the much slower pH independent hydration equilibria between I' and II' and I'' and II'' respectively are listed in Table I;<sup>13,14</sup> in the case of the hydration equilibria the individual rate constants are also included. One sees that these rate constants correspond to half-lives of  $>100$  sec. No oxalic acid catalysis of the hydration reactions is detectable. Therefore, in order to effectively isolate the rate of oxidation from the rates of the hydration equilibria, reaction conditions have to be selected for which the rate of oxidation is much higher than the equilibration rates. This requires an excess of oxidant concentration which is large enough to make the half-life of the oxidation  $<10$  sec. With this condition fulfilled, the kinetics are expected to correspond to the parallel oxidation of two substrates, namely I and II, yielding the same product, III.

Since the oxidation of Malachite Green by Cr(VI) proceeds to completion only in the presence of oxalic acid, the stopped-flow experiments can be carried out in two different ways. In the first case, one mixes a freshly prepared solution containing both Cr(VI) and oxalic acid with a second solution which contains the Malachite Green dye. Alternatively, a solution containing Malachite Green dye and oxalic acid is mixed with a Cr(VI) solution.

The first case is represented by Figure 2A. After mixing the two solutions one observes an almost instantaneous increase of  $A$  (460 nm) which is followed by a much slower build-up according to a first-order time dependence. The concomitant change of  $A$  (620 nm) does not obey any simple kinetic law during the initial stage of the oxidation but is much slower than the initial increase of  $A$  (460 nm); during the later stages of the reaction the decay of  $A$  (620 nm) becomes first order and occurs at a rate comparable to the corresponding build-up of  $A$  (460 nm).

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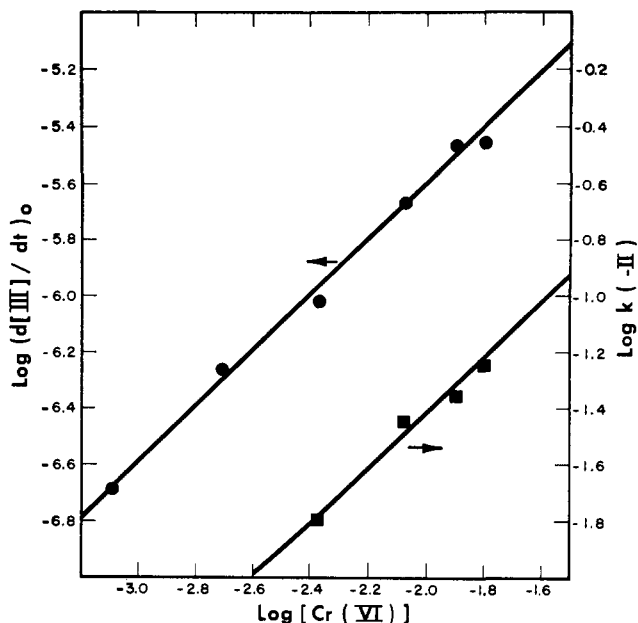
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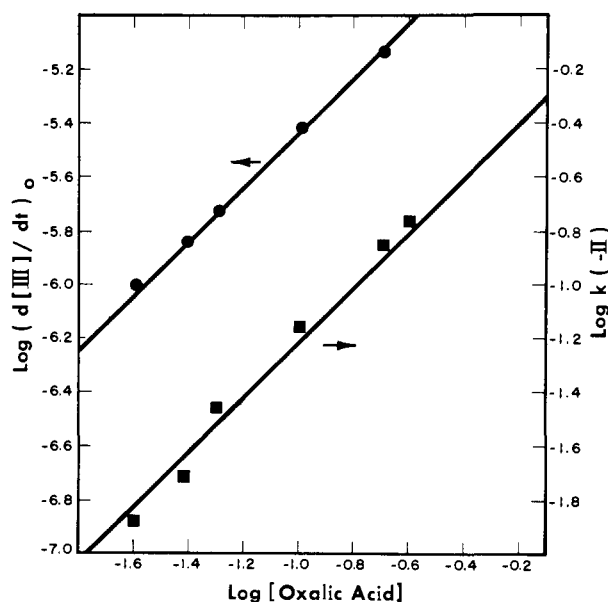
**Figure 2.** Time dependence of  $A$  (620 nm, (●) and 460 nm, (■)): (A) mixing of a solution containing Malachite Green dye with a second solution containing Cr(VI) and oxalic acid; (B) mixing of a solution containing Malachite Green dye and oxalic acid with a second solution containing Cr(VI). Conditions: [Malachite Green] =  $5.00 \times 10^{-5}$  M; [Cr(VI)] =  $2.50 \times 10^{-2}$  M; [oxalic acid] =  $5.00 \times 10^{-2}$  M; pH 3.0;  $T = +30^\circ$

The second case is depicted in Figure 2B. The initial rise of  $A$  (460 nm) is much slower than in the first experiment and occurs linearly with time; after this initial part is completed, the further increase of  $A$  (460 nm) again follows first-order kinetics. The initial value of  $A$  (620 nm) remains unchanged during the linear portion of the build-up of  $A$  (460 nm). After this induction period the further decay is exponential and takes place at a rate which is similar to the rate of the corresponding build-up of  $A$  (460 nm). In both experiments the final readings of  $A$  (460 nm) are identical, which indicates that the yields of III are likewise identical.

Comparing the results of the two experiments leads to the following conclusions. The initial, rapid oxidation is only observed if Cr(VI) and oxalic acid are allowed to equilibrate before the oxidation is carried out. This suggests that Cr(VI) and oxalic acid form a complex X which is the true oxidizing species. The fast initial rise in Figure 2A should therefore represent the rate of attack of X on the Malachite Green dye. This explanation is supported by the fact that the amount of Malachite Green which is oxidized in the fast process is proportional to the concentrations of both Cr(VI) and oxalic acid but independent of the Malachite Green dye concentration. In the Figure 2B case the oxidizing species X can only be formed after the mixing of the two solutions has taken place. Since the reaction proceeds

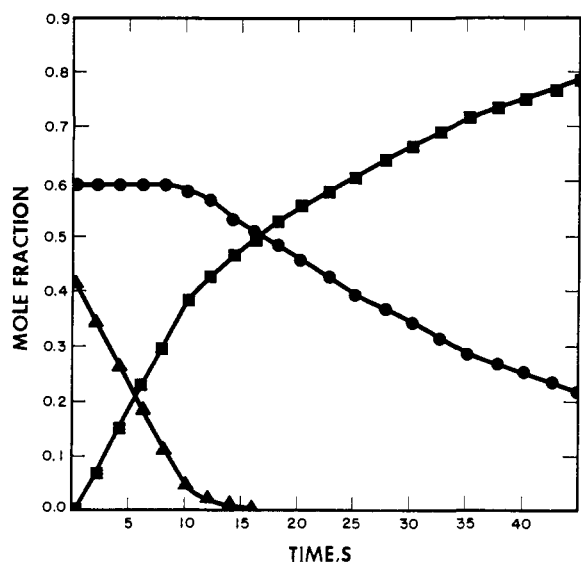


**Figure 3.** Effect of [Cr(VI)] on the pseudo-zeroth-order rate constant (●, left scale) and on the pseudo-first-order rate constant (■, right scale). The slopes of both straight lines are unity. Conditions: [Malachite Green] =  $1.00 \times 10^{-4}$  M; [oxalic acid] =  $5.00 \times 10^{-2}$  M; [ammonium sulfate] = 0.50 M; pH 3.0;  $T = +30^\circ$ .



**Figure 4.** Effect of oxalic acid on the pseudo-zeroth-order rate constant (●, left scale) and on the pseudo-first-order rate constant (■, right scale). The slopes of both straight lines are unity. Conditions: [Malachite Green] =  $1.00 \times 10^{-4}$  M; [Cr(VI)] =  $8.3 \times 10^{-3}$  M; [ammonium sulfate] = 0.50 M; pH 3.0;  $T = 30^\circ$ .

at a slower rate in this case and, moreover, initially follows a zeroth-order time dependence, the formation of X appears to be the rate-limiting factor, the oxidation in the first part of the reaction proceeding at the rate at which X is being formed. This is exemplified by Figures 3 and 4 which show the effect of the variation of the concentrations of Cr(VI) and oxalic acid, respectively, on the initial oxidation rate, as expressed by the rate of product formation,  $(d[\text{III}]/dt)_0$ . One recognizes that the pseudo-zeroth-order part of the oxidation is of first order with respect to either reactant.

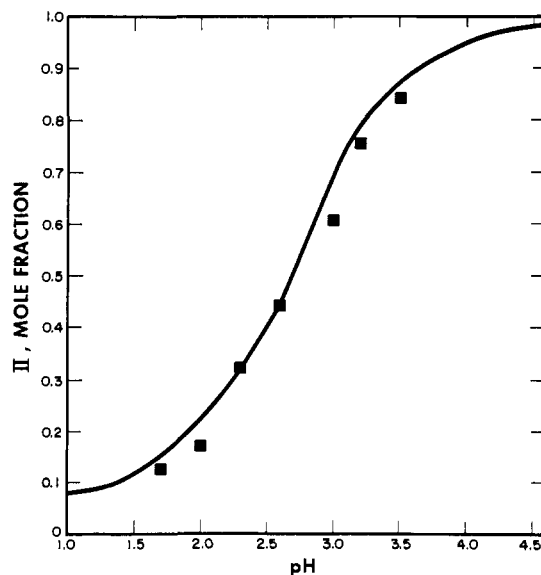


**Figure 5.** Time dependence of the composition of a typical reaction mixture: [I],  $\blacktriangle$ ; [II],  $\bullet$ ; [III],  $\blacksquare$ . Conditions: [Malachite Green] =  $2.50 \times 10^{-5} M$ ; [Cr(VI)] =  $5.00 \times 10^{-3} M$ ; [oxalic acid] =  $5.00 \times 10^{-2} M$ ; pH 3.0;  $T = +30^\circ$

Similarly, the pseudo-first-order rate constant for the disappearance of II,  $k(-II)$ , measured after termination of the induction period, increases linearly with the concentrations of either reactant. This identical effect on both the zeroth- and the first-order part of the reaction indicates that X is the true oxidizing species in both stages of the reaction. Therefore, experiments which are carried out according to Figure 2A yield information concerning the equilibrium concentration of X, while experiments according to Figure 2B yield the rate of reaction of Cr(VI) with oxalic acid with the formation of X. However, an answer as to the relative reactivities of the different Malachite Green species, I and II, toward X can only be obtained if the kinetic experiments are performed in the manner of Figure 2B. Consequently, all subsequent kinetic runs are carried out in this way.

Inspection of the plot of  $A$  (620 nm) in Figure 2B shows that the concentration of II remains virtually unchanged during the time corresponding to the zeroth-order build-up of III. This indicates that I is the species which is preferentially oxidized while II begins to be consumed only after I has been essentially used up. In addition, the constancy of [II] and the linear increase of [III] during the first part of the reaction are again indications that X reacts with I as fast as it is formed; the resulting low-steady-state concentration of X prevents its attack on the less reactive II species from being significant. Since the sum of [I], [II], and the product [III] must be a constant at all times, the time dependence of [I] may be calculated from that of the other two species. A typical example is given in Figure 5, which shows that the transition from zeroth- to first-order kinetics in the formation curve of III corresponds to the time at which almost all the initially present I has been oxidized.

In order to verify the relationship between the zeroth-order part of the reaction and the initial concentration of the species I, a series of experiments was done in which solutions of Malachite Green and



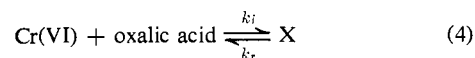
**Figure 6.** Kinetically determined composition of the Malachite Green dye solution at different acidities. Same conditions as in Table II. The solid curve is calculated from the data listed in Table I.

oxalic acid were equilibrated at known pH and subsequently rapidly mixed with a Cr(VI) solution strongly buffered at pH 3.0. The oxidation occurs at pH 3.0, but the relative amounts of species I and II depend on the equilibration pH. At each equilibration pH the concentration of III at the break in its formation curve is taken as corresponding to the concentration of I at the start of the reaction. The initial mole fractions of I and II are then calculated and compared with the corresponding values calculated from the equilibrium constants of Table I by means of eq 3. The results,

$$\frac{[II]}{[II] + [I]} = \frac{1 + K_1[H^+]}{1 + K_1[H^+] + 1/K_4 + K_1K_2[H^+]} \quad (3)$$

compared in Figure 6, show satisfactory agreement between our kinetic and equilibrium calculations, justifying our interpretation of the kinetic behavior.

Table II shows the kinetic results which are obtained from the variation of the ratio [I]/[II] within a factor of 10. As required by our kinetic model, the initial rate of oxidation,  $(d[III]/dt)_0$ , is invariant with respect to the composition of the Malachite Green solution. Therefore, the pseudo-zeroth-order part of the reaction indeed represents the forward rate of the complex-forming equilibrium according to eq 4. Consequently,



division of the initial rate by the total concentrations of both Cr(VI) and oxalic acid and accounting for the stoichiometric factor according to eq 2 yields a rate constant for the forward reaction with respect to X of  $k_f = 4 \times 2.96 \times 10^{-3} M^{-1} \text{sec}^{-1} = 11.84 \times 10^{-3} M^{-1} \text{sec}^{-1}$  at pH 3.0.

The pseudo-first-order rate constants for the formation of III and the disappearance of II are also approximately constant with the ratio  $k(III)/k(-II)$  being greater than one. This behavior indicates that as soon as the concentration of the more reactive species, [I], drops to a low level, the oxidation step becomes

**Table II.** Effect of the Equilibrium Composition of the Malachite Green Solution<sup>a</sup>

pH <sup>b</sup>	([II]/([II] + [I])) <sub>0</sub> <sup>c</sup>	Zeroth-order part (d[III]/dt) <sub>0</sub> × 10 <sup>7</sup> , M sec <sup>-1</sup>	First-order part		k(III)/k(-II)
			k(III) × 10 <sup>2</sup> , sec <sup>-1</sup>	k(-II) × 10 <sup>2</sup> , sec <sup>-1</sup>	
1.7	0.122	10.41			
2.0	0.166	6.40	4.33	3.30	1.31
2.3	0.320	6.18	2.43	2.39	1.02
2.6	0.441	7.36	2.10	2.03	1.03
3.0	0.602	7.56	2.89	2.31	1.25
3.2	0.753	7.72	3.01	1.98	1.52
3.5	0.840	6.19	3.15	2.66	1.18
		Av 7.40	2.99	2.44	1.22
Av/([Cr(VI)] <sub>T</sub> [oxalic acid] <sub>T</sub> )		2.96 × 10 <sup>-3</sup> M <sup>-1</sup> sec <sup>-1</sup>	120 M <sup>-2</sup> sec <sup>-1</sup>	98 M <sup>-2</sup> sec <sup>-1</sup>	

<sup>a</sup> [Malachite Green]<sub>T</sub> = 2.5 × 10<sup>-5</sup> M; [oxalic acid]<sub>T</sub> = 5.0 × 10<sup>-2</sup> M; [Cr(VI)]<sub>T</sub> = 5.0 × 10<sup>-3</sup> M; T = 30°; pH after mixing 3.0; buffer = potassium acid phthalate, 0.2 M. <sup>b</sup> pH at which the Malachite Green solution is equilibrated prior to mixing. <sup>c</sup> Calculated from the values of Table I according to eq 3.

**Table III.** Relative Initial Rates<sup>a</sup>

Mixing pH	([II]/([II] + [I])) <sub>0</sub>	V(-I) × 10 <sup>7</sup> M sec <sup>-1</sup> <sup>b</sup>	V(-II) × 10 <sup>7</sup> M sec <sup>-1</sup> <sup>b</sup>	V <sub>t</sub> × 10 <sup>7</sup> M sec <sup>-1</sup> <sup>b</sup>	V(-I)/V(-II)	V(-I)/V <sub>t</sub>	V(-II)/V <sub>t</sub>
1.7	0.122	94.4	0.749	7.40	126	12.8	0.101
2.3	0.320	73.2	1.96	7.40	37.4	9.89	0.265
3.0	0.602	42.7	3.69	7.40	11.6	5.77	0.499
3.2	0.752	26.7	4.61	7.40	5.80	3.61	0.623
3.5	0.840	17.2	5.15	7.40	3.34	2.32	0.696

<sup>a</sup> Conditions are the same as for Table II. <sup>b</sup> V(-I) = k(-I)[I]<sub>0</sub>; V(-II) = k(-II)[II]<sub>0</sub>; V<sub>t</sub> = av(d[III]/dt)<sub>0</sub>.

rate limiting also for this substrate. Consequently, the pseudo-first-order part represents the parallel oxidation of I and II with the attack of X as the rate-limiting step.

We can estimate the rate constant for the oxidation of I, k(-I), by utilizing the first-order part of the curves of the material balance plot of Figure 5. At several concentrations, one calculates the mole fraction of I from the II and III values. At each such point, one also obtains d[III]/dt directly from the plot. Then, from the relationship according to eq 5 and k(-II) =

$$d[\text{III}]/dt = k(-\text{I})[\text{I}] + k(-\text{II})[\text{II}] \quad (5)$$

2.44 × 10<sup>-2</sup> sec<sup>-1</sup> from Table II, an average first-order rate constant, k(-I) = 0.43 sec<sup>-1</sup>, is obtained. The relative reactivities of the dye species are then given by k(-I)/k(-II) = 17.6. Additionally, we can calculate the actual initial velocities as shown in Table III. Over the entire range of compositions shown, the initial velocity of oxidation of I remains greater than the velocity of formation of X, making the formation of the latter rate determining. Of course, at very small initial concentrations of I as well as upon its exhaustion during the course of a reaction, V(-I), the rate of oxidation of I must eventually fall below the rate of formation of X. As the pH gets higher, the zeroth-order portion gets shorter and the transition from zeroth- to first-order kinetics gets less abrupt. The rate of oxidation of II is always less than the rate of formation of X even at a mole fraction of 1, which means that the attack of X on II is always the slowest process for the conditions shown in Tables II and III.

If the concentration of the dye is varied over a wide range, some effects on the values of k<sub>t</sub> and k(-II) are observed; while k<sub>t</sub> shows a tendency to increase at higher concentrations, k(-II) tends to decrease. This behavior may be caused by a change in the degree of association of the Malachite Green species which occurs even at fairly low concentration.<sup>15</sup> Alter-

natively, since k<sub>t</sub> is obtained from the zeroth-order oxidation rate, the concentration of X being unknown, the oxidation step should become rate limiting at low dye concentration resulting in a decrease in the value of k<sub>t</sub>. On the other hand, the formation rate of X may limit the value of k(-II) at high dye concentrations.

The effect of acidity on the rate of oxidation may be established by equilibrating the Malachite Green-oxalic acid solution at a known pH and mixing it with a Cr(VI) solution of identical pH. To eliminate the effects of changing ionic strength, the oxidation is carried out with a constant large excess of ammonium sulfate. In the acidity range examined, the shape of the kinetic curves remains unchanged. In each case one observes a zeroth-order rise of [III] which changes to first order in the second stage of the reaction. Similarly, one finds again that [II] remains initially unchanged and subsequently decays according to a first-order law. Both the zeroth-order and the first-order part of the reaction are acid catalyzed. However, the apparent order with respect to [H<sup>+</sup>] is higher for the first-order part of the reaction than for the initial zeroth-order part. This different acidity dependence agrees with our kinetic model which requires a change of the rate-limiting step coinciding with the change of the kinetic order for the formation of III. These two different processes are likely to show a different dependence on acidity. Moreover, the acidity dependence of the oxidation step should also contain the acidity dependence of the preceding formation of the oxidizing species. If both processes are acid catalyzed, the apparent effect of acidity should therefore be stronger for this part of the reaction where the oxidation step becomes rate limiting, which is in accordance with the experimental results.

Table IV summarizes the effect of acidity on the

(15) W. H. J. Stork, G. J. M. Lippits, and M. Mandel, *J. Phys. Chem.*, **76**, 1772 (1972).

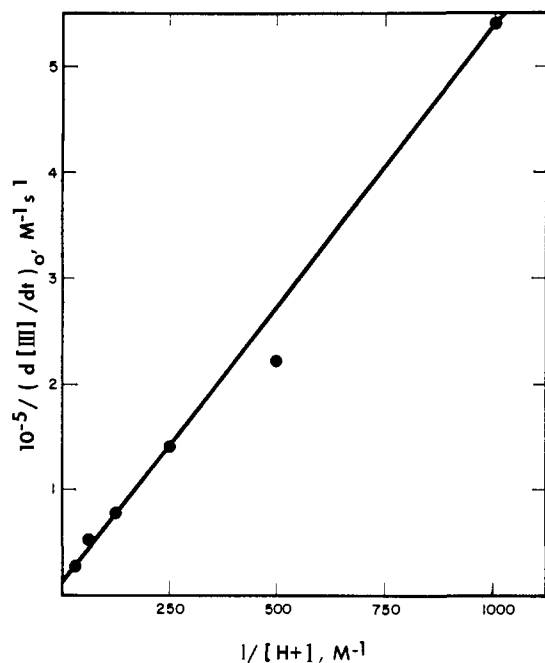


Figure 7. Graphical determination of the equilibrium constant  $K'$  with the data taken from Table IV.

Table IV. Effect of Acidity on the Zeroth-Order Part of the Reaction<sup>a</sup>

$[H^+] \times 10^3$ $M$	$(d[III]/dt)_0$ $\times 10^8, M$ $sec^{-1}$	$((d[III]/dt)_0 / [H^+]) \times 10^8,$ $sec^{-1}$	$((d[III]/dt)_0([H^+] + K') / [H^+]) \times 10^4, M sec^{-1}$
31.6	37.7	1.19	1.01
15.8	19.2	1.21	0.84
7.94	12.1	1.51	0.93
3.98	7.14	1.79	1.02
2.00	4.50	2.25	1.23
1.00	1.85	1.85	1.00
			Av 1.01

$$Av/([Cr(VI)]_T[oxalic acid]_T): 2.42 \times 10^{-1} M^{-1} sec^{-1}$$

<sup>a</sup> [Malachite Green]<sub>T</sub> =  $1.0 \times 10^{-4} M$ ; [oxalic acid]<sub>T</sub> =  $5.00 \times 10^{-2} M$ ; [Cr(VI)]<sub>T</sub> =  $8.3 \times 10^{-3} M$ ; [ammonium sulfate] =  $0.50 M$ ;  $T = 30^\circ$ .

zeroth-order part of the reaction. The decrease of the values in column 3 with increasing acidity implies an apparent order of less than unity with respect to  $[H^+]$  for the formation of the complex X. The acidity dependence may be quantitatively evaluated from a plot of the zeroth-order rate constant *vs.* the hydrogen ion concentration in reciprocal coordinates according to Figure 7. With slope = 530 sec and intercept =  $1 \times 10^4 M^{-1} sec$ , a value of slope/intercept,  $K' = 0.053 M$ , is calculated which agrees well with the dissociation constant for oxalic acid,  $K_a = 0.059$ .<sup>16</sup> It has been established that the undissociated form of oxalic acid is required for the formation of complexes with Cr(VI).<sup>17,18</sup> The data in column 4 are corrected for the experimentally determined  $K'$  resulting in values invariant with acidity. The apparent acidity dependence may therefore be satisfactorily explained by the uncatalyzed reaction of Cr(VI) with the undissociated oxalic acid.

(16) "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967-1968.

(17) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 9073 (1972).

(18) G. V. Bakore and C. L. Jain, *J. Inorg. Nucl. Chem.*, **31**, 805 (1969).

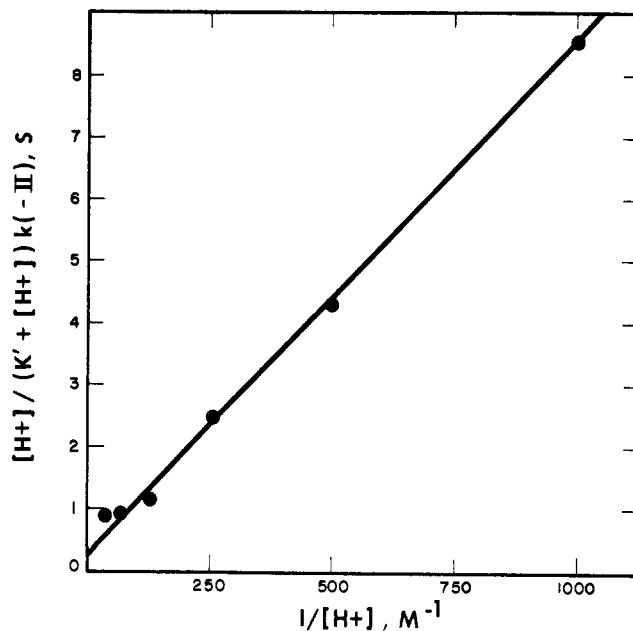


Figure 8. Graphical determination of the equilibrium constant  $K''$  with the data taken from Table V.

Division of the average of the corrected values of Table IV by  $[Cr(VI)]_T$  and  $[oxalic acid]_T$  and accounting for the stoichiometric factor yields the acidity independent rate constant,  $k_f^0 = 4 \times 0.242 M^{-1} sec^{-1}$ , for the formation of X. Therefore, the rate law according to eq 6 is obtained for the zeroth-order part of the re-

$$d[X]/dt = k_f^0 [Cr(VI)]_T [oxalic acid]_T [H^+] / ([H^+] + K') \quad (6)$$

action. The effect of acidity on  $k(-II)$  is shown in Table V. According to column 3, the correction for the

Table V. Effect of Acidity on the First-Order Part of the Oxidation<sup>a</sup>

$[H^+] \times 10^3$ $M$	$k(-II) \times 10^2, sec^{-1}$	$k(-II)([H^+] + K') / [H^+], sec^{-1}$	$k(-II)([H^+] + K') / ([H^+] + K'') / [H^+]^2, sec^{-1}$
31.6	396	1.06	2.17 <sup>b</sup>
15.8	231	1.01	3.12
7.94	106	0.814	4.20
3.98	25.6	0.367	3.41
2.00	7.45	0.205	3.59
1.00	2.00	0.108	3.67
			Av 3.60

$$Av/([Cr(VI)]_T[oxalic acid]_T): 8.68 \times 10^8 M^{-2} sec^{-1}$$

<sup>a</sup> Conditions as in Table IV. <sup>b</sup> This value is not included in the average.

dissociation of oxalic acid is not sufficient to account for the acidity dependence. Since the residual effect of acidity amounts to an apparent order with respect to  $[H^+]$  of less than unity, one has to assume that an additional protolytic equilibrium becomes kinetically important after the rate-limiting step changes from the formation of X to the attack of X on the substrate. The numerical value of this additional equilibrium constant may be obtained by plotting the reciprocal of the column 3 values,  $[H^+]/(K' + [H^+])k(-II)$  *vs.*  $1/[H^+]$ . This plot is shown in Figure 8. With a slope

=  $8.28 \times 10^{-3} M$  sec and intercept = 0.25 sec, one obtains a value of slope/intercept = 0.033  $M$  for the constant of the second protolytic equilibrium,  $K''$ . Comparison with the constants of the protolytic equilibria listed in Table I suggests that this kinetically determined constant represents the equilibrium  $II'' \rightleftharpoons II' + H^+$ . The fourth column of Table V incorporates this additional correction and, after division by  $[Cr(VI)]_T$  and  $[oxalic\ acid]_T$ , yields the acidity independent rate constant,  $k(-II)^0 = 8.68 \times 10^3 M^{-2} sec^{-1}$ . Consequently, the rate law for the oxidation of II after termination of the induction period is described by eq 7. The rate law, eq 7, may alterna-

$$-d[II]/dt = k(-II)^0[II][Cr(VI)]_T \times [oxalic\ acid]_T[H^+]^2/([H^+] + K')(H^+ + K'') \quad (7)$$

tively be interpreted as the acidity independent attack of X on the  $II''$  species or the attack of a protonated form of X on the  $II'$  species; a decision based solely on kinetic experiments is not possible.

The effect of acidity on  $k(-I)$  was not investigated because of the large uncertainty involved in the determination of  $k(III)/k(-II)$ . It is therefore not possible to write an explicit rate equation which holds for the oxidation of I for the entire acidity range.

In order to arrive at a final description of the overall rate equation governing the oxidation, we can write the following simplified eq 8 from which we omit the effects of acidity.

$$d[X]/dt = k_f^0[Cr(VI)]_T[oxalic\ acid]_T - k_r^0[X] - 4k(-I)^0[I][X] - 4k(-II)^0[II][X] \quad (8)$$

According to our experimental results, the application of the Bodenstein approximation with regard to X appears to be justified, and one can obtain the steady-state concentration,  $X_{ss}$ , given by eq 9. The rate law

$$[X]_{ss} = k_f^0[Cr(VI)]_T[oxalic\ acid]_T/(k_r^0 + 4k(-I)^0[I] + 4k(-II)^0[II]) \quad (9)$$

with respect to the formation of III is then expressed by eq 10 which includes the oxalic acid acidity dependence

$$d[III]/dt = k_f^0[Cr(VI)]_T[oxalic\ acid]_T \times \frac{[H^+]}{[H^+] + K'} \times \frac{k(-I)^0[I] + k(-II)^0[II]}{k_r^0 + 4k(-I)^0[I] + 4k(-II)^0[II]} \quad (10)$$

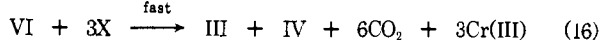
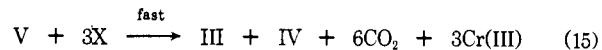
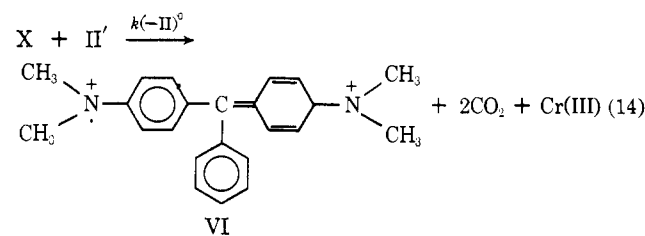
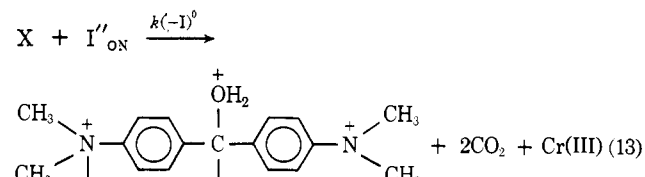
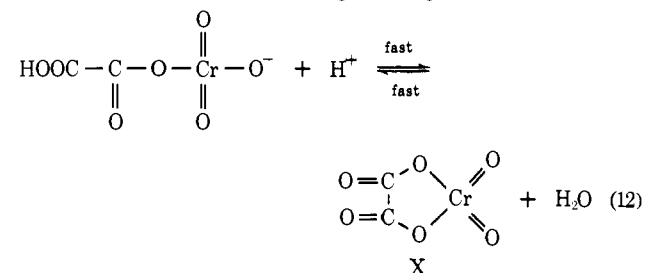
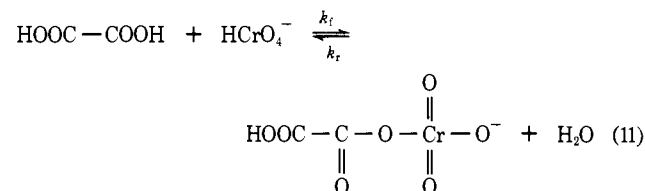
but omits the acidity dependence with respect to  $K''$ , since we are unable to include a function for the acidity dependence governing the oxidation rate of the I species. This rate equation is of zeroth order with respect to the Malachite Green species, provided that  $k(-I)^0[I] + k(-II)^0[II] \gg k_r^0/4$  and changes to first order if  $k_r^0$  becomes predominant. Similarly, the rate with respect to II should be negligible as long as  $k(-I)^0[I] > k(-II)^0[II]$ , which is in agreement with the experimentally observed induction period for II.

## Discussion

The tendency of Cr(VI) to form complexes with various anions is well established.<sup>19</sup> The strong enhancement of the oxidation of 2-propanol, however, is observed only for the Cr(VI)-oxalic acid complex as well as for the complexes of Cr(VI) with a variety of organic acids, notably hydroxy acids and picolinic acid.<sup>20</sup>

(19) J. K. Beattie and G. P. Haight, *Progr. Inorg. Chem.*, **17**, 93 (1972).

## Scheme IV



The results of this study confirm the participation of a Cr(VI)-oxalic acid complex in the oxidation of the Malachite Green species I and II. Therefore, the action of oxalic acid is evidently not limited to 2-propanol but appears to occur with a variety of different substrates. However, the Malachite Green species seems to be especially susceptible to oxidation by this complex as may be inferred from the rather high value of  $k(-II)^0 = 8.68 \times 10^3 M^{-2} sec^{-1}$ . The I species is oxidized even faster; assuming that the same acidity dependence as for the II species holds, a value of  $k(-I)^0 = 1.3 \times 10^5 M^{-2} sec^{-1}$  is estimated. These rate constants may be compared with the reported value of  $k(-2-propanol)^0 = 8.78 M^{-2} sec^{-1}$  at 20°.<sup>8</sup>

The reaction sequence given by Scheme IV is consistent with both the stoichiometric and the kinetic results. According to the experimentally observed acidity dependence of  $k_f$ , the rate-limiting step in the formation of the complex X involves the reaction of undissociated oxalic acid with a Cr(VI) species. Since the dissociation constant of chromic acid is 3.3 at 30°,<sup>21</sup> the concentration of undissociated chromic acid is entirely negligible within the acidity range of our experiments; owing to the low total concentration of Cr(VI), the formation of dimeric Cr(VI) species is

(20) F. Hasan and J. Roček, *J. Org. Chem.*, **38**, 3812 (1973).

(21) J. Y. P. Tong and R. L. Johnson, *Inorg. Chem.*, **5**, 1902 (1966).



likewise unimportant. Consequently, practically the entire Cr(VI) exists in the form of the acid chromate anion, and the rate-limiting step in the formation of the complex may be expressed according to eq 11. Since this reaction is relatively slow, it may be followed by a rapid cyclization according to eq 12 which leads to the cyclic anhydride, the existence of which has been postulated in the oxidation of 2-propanol.<sup>8</sup> This reaction requires the participation of a proton and thus accommodates the acidity dependence of the oxidation step which is observed in the case of the II species.

In this connection it is of interest that also in the case of the oxidation of 2-propanol the experimentally obtained rate equation does not contain a  $[H^+]$  term after accounting for the dissociation equilibrium of oxalic acid. However, the proposed mechanism which involves a cyclic anhydride as a reaction intermediate requires the participation of an additional proton which is therefore obviously not involved in the rate-limiting step.<sup>8</sup>

The cyclic anhydride, X, is then the oxidizing agent which attacks the Malachite Green species I and II. The different protonation levels of both Malachite Green species according to Schemes I and II are expected to exhibit rather different stabilities toward attack by an oxidizing agent. Since every oxidation involves the removal of electrons, the species which carry a higher positive charge are *a priori* expected to be less easily oxidized.

In the case of the I species, the higher protonated form I'' is predominant within the entire acidity range investigated; the ratio  $[I'']/[I']$  increases from 32 at pH 3.0 to >1000 at pH 1.5. This would require empirical third-order rate constants of up to  $10^8 M^{-2} sec^{-1}$  for the oxidation of the I' form. Since the formation of the stable oxidation products III and IV requires the consecutive attack by several oxidizing species which presumably occurs at an even higher velocity, the overall reaction with the I' species as a substrate would become rather fast. It appears therefore more likely that the reaction occurs *via* an attack on the I'' form. The oxidation of I'' is presumably facilitated by the repulsion of the two negative charges which should result in a more negative activation entropy in this case.

In the case of the II species, the ratio of the equilibrium concentrations,  $[II'']/[II']$ , varies from 0.03 at pH 3.0 to 0.95 at pH 1.5, which means that the contribution of both protonation levels is comparable within the acidity range considered. As has been shown, the acidity dependence of  $k(-II)$  may be either explained in terms of an acid-catalyzed attack of X on the II' form or the uncatalyzed attack of X on the II'' form. No decision is possible on kinetic grounds in favor of either possibility.

The stoichiometry, according to eq 1, shows that four Cr(VI) are required to oxidize one Malachite Green to the products III and IV. Since the oxidation involves the transfer of four electrons, the reaction is most likely to proceed *via* four consecutive one-electron transfers with respect to the Malachite Green substrate. Simultaneously, the oxalic acid part of the cyclic anhydride is oxidized *via* a two-electron transfer with formation of two CO<sub>2</sub> and one Cr(III) for each step.

According to eq 13 and 14, the probable site of the

initial one-electron oxidation of the Malachite Green species is at the free electron pair of an unprotonated nitrogen. One sees that this reaction mode excludes an oxidative attack on the II'' as well as on the I<sub>NN''</sub> forms, since these species do not possess unprotonated nitrogen as a possible site of attack by the oxidant. Since the I' form may be excluded because of the restriction imposed by the position of the protolytic equilibrium, the I<sub>ON''</sub> and the II' are the most likely species to be oxidized. The higher resistance of the II species toward oxidative attack is readily explained by the reduction of the electron density at the unprotonated nitrogen due to resonance.

The abstraction of one electron yields the hydrated or unhydrated radical cations V and VI, respectively, which are then subject to rapid further oxidation leading to a complete breakdown of the Malachite Green entity as is demonstrated by the nature of the reaction products III and IV. The assumption that the following oxidation steps, which are summarized by eq 15 and 16, are fast is supported by the fact that no experimental evidence for any reaction intermediates could be obtained. No transient spectra are observed and no induction period for the appearance of the end-product, III, is found.

Interestingly, it has been deduced from the negative results of "crossing" experiments that the entire reaction sequence occurs intramolecularly. To account for this observation, a hypothetical cyclopropyl reaction intermediate has been suggested.<sup>4</sup> However, this apparent intramolecular mode of reaction may be caused by the rather high reaction velocities which may prevent short-lived reaction intermediates from leaving the solvent cage.

In the case of the oxidation of 2-propanol by Cr(VI) and oxalic acid, a reaction mechanism has been suggested which involves a two-electron oxidation of the alcohol in conjunction with a one-electron oxidation of oxalic acid.<sup>8</sup> Although the stoichiometry which is observed in our study may be reconciled with a two-electron oxidation of the Malachite Green, it is, however, difficult to visualize this reaction mode for an attack on the unshared electron pair of the nitrogen. On the other hand, if the attack occurs at the hydroxyl function, which is possible only in the case of the I<sub>NN''</sub> species, the reaction *via* a transient Cr(VI) ester involving a two-electron oxidation cannot be excluded. However, the high rate of the oxidation step makes an intermediate ester formation rather unlikely. Moreover, the mechanism which is valid in the case of 2-propanol involves an ester formation *via* S<sub>N</sub>2 reaction. This reaction path is obviously disfavored in the case of the tertiary carbinol I in comparison to an S<sub>N</sub>1 ester mechanism for which the cation II' is a necessary intermediate. Hence, II being more stable toward oxidation than I, the former cannot be the required intermediate in an oxidation *via* a transient Cr(VI) ester. Furthermore, we have observed that leuco Malachite Green, which is structurally closely related to the alcohol I except for the missing hydroxyl function, is oxidized at practically the same rate as the I species.<sup>22</sup> These considerations make a two-electron mechanism for the oxidation of Malachite Green highly improbable.

(22) A. Granzow, unpublished results.