small amount of AIBN were dissolved in the solvent under a nitrogen atmosphere. The apparatus was closed and irradiated with a G.E. sun lamp for up to 22.5 hr. Samples of the solution were then analyzed by glpc on a 6 × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 95°.

For experiments at 0.3 *M* the same amounts of reactants were dissolved in 25 ml of solvent in a smaller apparatus.

B. Neat. Crotononitrile or isocrotononitrile (3.35 g, 0.05 mol) was placed in a Pyrex photolysis apparatus of appropriate size so that the cold finger reached into the liquid. To this was added 1.84 g (0.017 mol) of *tert*-butyl hypochlorite and a small amount of AIBN. The mixture was irradiated for up to 21 hr while being stirred magnetically and cooled by the cold finger. Samples of the mixture were then analyzed by glpc as described above.

Reaction of *tert*-Butyl Hypochlorite with Methyl Crotonate and Methyl Isocrotonate at 25°. Methyl crotonate and methyl isocrotonate were allowed to react with *tert*-butyl hypochlorite both neat and in solution in a manner analogous to that used for crotononitrile and isocrotononitrile. Glpc analysis of the products was performed on a 6 ft × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 110°.

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Registry No.—*trans*-1-Chloro-2-butene, 4894-61-5; *cis*-1-chloro-2-butene, 4628-21-1; *trans*-1-chloro-2-pentene, 6261-25-2; *cis*-1-chloro-2-pentene, 6261-19-4; *trans*-1-chloro-4,4-dimethyl-2-pentene, 19146-05-5; *cis*-1-chloro-4,4-dimethyl-2-pentene, 19146-06-6; triphenyltin hydride, 892-20-6; methyl γ-chlorocrotonate, 999-54-2; methyl crotonate, 623-43-8; *tert*-butyl hypochlorite, 507-40-4; methyl γ-chloroisocrotonate, 999-53-1; methyl isocrotonate, 4358-59-2; γ-chlorocrotononitrile, 7659-46-3; γ-chloroisocrotononitrile, 20592-22-7; *cis*-crotononitrile, 1190-76-7; *trans*-crotononitrile, 627-26-9; γ-chloro-*N,N*-dimethylcrotonamide, 51830-58-1; methyl γ-bromocrotonate, 6000-00-6.

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Three-Electron Oxidations. VII. The Pre-Steady-State Phase of the Chromic Acid Oxidation of Oxalic Acid[1,2]

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The study of the initial rates of formation of chromium(III) in the chromic acid oxidation of oxalic acid shows the absence of an induction period; this result is incompatible with any mechanism following the general scheme Cr(VI) → Cr(V) → Cr(III), according to which all chromium would pass through the chromium(V) state. In agreement with the previously proposed three-electron oxidation mechanism, the initial rate of formation of chromium(III) is never lower than one-half of the rate of reduction of chromium(VI). The initial rates of formation of chromium(III) as well as the maximum concentration of chromium(V) formed depend on both total chromic acid concentration and on the acidity. The results show that the $\cdot CO_2H$ radicals react predominantly with chromium(VI) to yield CO_2 and chromium(V) at high chromic acid concentrations and acidities, but undergo extensive bimolecular dimerization at low chromic acid concentrations and acidities.

In a recent paper from this laboratory[3] it was shown that during the chromic acid oxidation of oxalic acid, a long-lived chromium(V) intermediate is formed in rather large concentrations. The reaction can be described as having two distinct phases. The initial phase is characterized by a decrease in the concentration of chromium(VI) and a rapid buildup of the chromium(V) intermediate. During the second phase of the reaction, after the concentration of chromium(V) has reached its maximum, the concentrations of both chromium(V) and chromium(VI) decrease approximately in parallel, and a quasi-steady-state concentration of chromium(V) with respect to the concentration of chromium(VI) is established and maintained.

The purpose of this study was to obtain answers to two basic questions concerning the mechanism of reaction: (1) does all, or only a fraction, of the total chromium pass through the chromium(V) stage; (2) do all, or only a fraction of the free radicals undergo further oxidation?

The oxidation of oxalic acid takes place by two routes, namely, through a 1:1 and a 2:1 oxalic acid–chromic acid complex.[4] The mechanism for the second route, which (except for very low oxalic acid concentrations) is by far the

Scheme I

$$2(CO_2H)_2 + Cr(VI) \xrightarrow{k_1} 3CO_2 + \cdot CO_2H + Cr(III) \quad (1)$$

$$\cdot CO_2H + Cr(VI) \xrightarrow{k_2} CO_2 + Cr(V) \quad (2)$$

$$(CO_2H)_2 + Cr(V) \xrightarrow{k_3} 2CO_2 + Cr(III) \quad (3)$$

$$2\cdot CO_2H \xrightarrow{k_4} (CO_2H)_2 \quad (4)$$

more important one, is given in Scheme I.[4a] This mechanism requires that at least one-half or a greater fraction (depending on the importance of reaction 4 relative to reaction 2) of chromium(VI) is reduced directly to chromium(III) without passing through a chromium(V) stage.[5]

Mechanisms in which chromium(VI) is either reduced stepwise in a series of one-electron reductions or in which chromium(IV) formed in a two-electron reduction is reoxidized to chromium(V) lead to the same general scheme (Scheme II) according to which all chromium passes through the chromium(V) stage. If a reaction during which chromium(V) accumulates in appreciable amounts follows Scheme II, the initial rate of chromium(III) formation should be zero at time $t = 0$; *i.e.*, an induction period for the formation of chromium(III) should be observed.

Scheme II

$$Cr(VI) \longrightarrow Cr(V) \longrightarrow Cr(III)$$

The determination of the initial rate of formation of chromium(III) should thus permit us to distinguish between the mechanisms of Schemes I and II and to assess the importance of the bimolecular free radical process (reaction 4) in the mechanism of Scheme I.

Results and Discussion

The rate of formation of chromium(III) can be followed spectrophotometrically at about 600 nm, where the absorptions of both chromium(VI) and chromium(V) are negligible.[3] On the other hand, there is no region of the spectrum in which the concentration of either chromium(VI) or of chromium(V) could be determined without interference from the other species. The concentration of chromium(VI) and its rate of change therefore cannot be determined directly from spectrophotometric measurements.

During the pre-steady-state phase of the reaction the concentration of chromium(V) increases rapidly; consequently, the rates of formation of chromium(III) and of reduction of chromium(VI) may differ considerably. On the other hand, the concentration of chromium(V) changes only slowly during the second phase and the rates of formation of chromium(III) and of the reduction of chromium(VI) are therefore very approximately equal. Thus, if the reaction is carried out under pseudo-first-order conditions, the rate constant of chromium(III) formation in the second phase of the reaction thus provides a satisfactory measure of the rate of reduction of chromium(VI) throughout the reaction. Hence, the ratio of the first-order rate constants for the chromium(III) formation in the initial and in the second phase of the reaction (k_i/k_s) can be used as an adequate measure of the rate of chromium(III) formation relative to chromium(VI) reduction at the beginning of the reaction.

Figure 1 shows typical examples of plots of the absorption at 600 nm *vs.* time used in this study. The results clearly show that the rate of chromium(III) formation indeed changes during the course of the reaction, with the initial rate being considerably slower than the rate in the second phase. In both regions reasonably good straight lines for log (absorbance) *vs.* time plots are obtained, indicating that the rate of chromium(III) formation is first order in the overall concentration of chromium(VI). Table I summarizes the values for k_i (pseudo-first-order rate constants for the initial part of the reaction), k_s (rate constants for the pseudo-steady-state phase), and the ratio k_i/k_s.

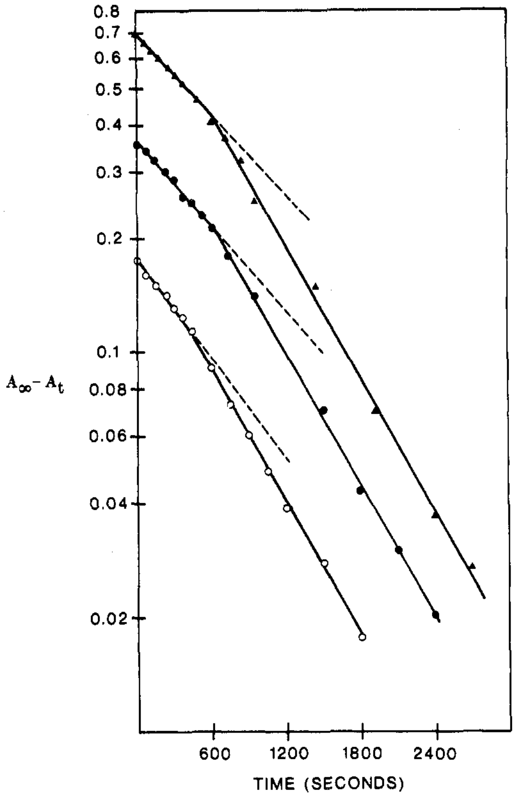

Figure 1. Pseudo-first-order rate plots for the formation of chromium(III) at 25°: oxalic acid 0.115 *M;* perchloric acid 0.388 *M.* Initial concentrations of Cr(VI): ○, 8.12 × 10^{-4} *M;* □, 2.03 × 10^{-3} *M;* △, 4.06 × 10^{-3} *M.*

The results show that the value of k_i/k_s depends both on the concentration of chromic acid and on acidity and varies between 0.50 and 0.85. Under no conditions has a genuine induction period for the formation of chromium(III) been observed. *The results thus are incompatible with any mechanism which would require that all chromium passes through a chromium(V) stage (Scheme II).*

Table I
Rates of Formation of Chromium(III) at 25°

A. Oxalic Acid[a] 0.115 *M;* Perchloric Acid 0.388 *M*

Cr(VI), 10^3 *M*	10^3 k_i, sec^{-1}	10^3 k_s, sec^{-1}	k_i/k_s
0.812	0.995	1.24	0.80
2.03	0.845	1.24	0.68
4.06	0.782	1.24	0.63
8.12	0.746	1.22	0.61
22.7	0.625	1.22	0.51
40.6	0.621	1.24	0.52

B. Chromium(VI) 4.06 × 10^{-3} *M;* Oxalic Acid[a] 0.115 *M*

$HClO_4$, 10^2 *M*	10^4 k_i, sec^{-1}	10^4 k_s, sec^{-1}	k_i/k_s
0.97	0.302	0.354	0.85
2.4	1.23	1.48	0.83
4.8	2.72	3.62	0.75
9.7	4.98	7.02	0.71
24.2	7.27	11.2	0.68
38.8	7.87	12.4	0.63
48.4	7.76	13.0	0.60
96.9	6.56	11.7	0.56

[a] Total (not corrected for dissociation).

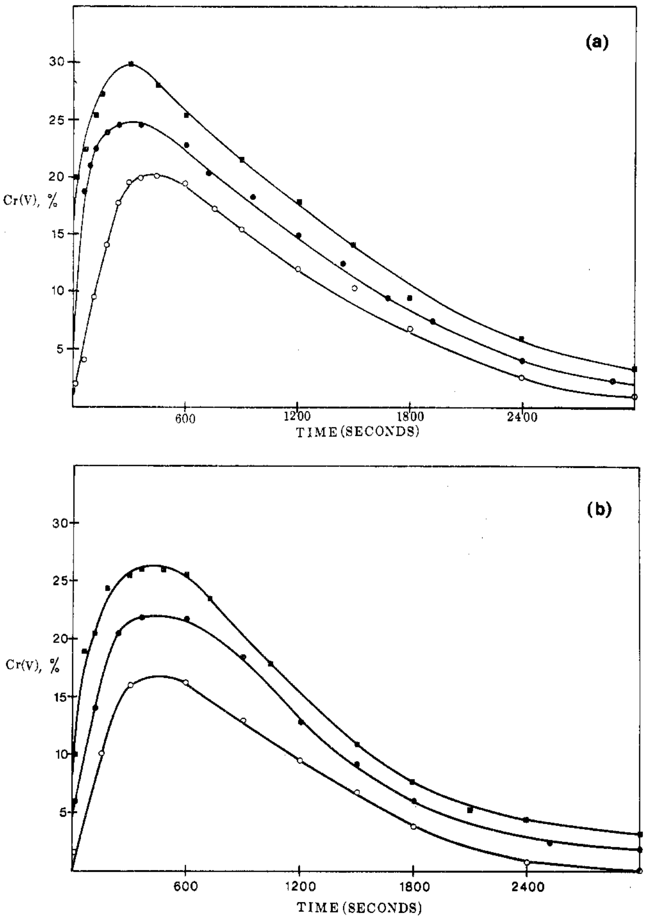

Figure 2. Formation of chromium(V). Initial concentration of Cr(VI): ○, 8.12×10^{-4} *M*; ●, 4.06×10^{-3} *M*; ■, 8.12×10^{-3} *M*. $HClO_4$: a, 0.388 *M*; b, 0.242 *M*.

The observation that the values of k_i/k_s approach the value of 0.50 and depend on reaction conditions is in full agreement with the proposed three-electron mechanism (Scheme I). The results further show that bimolecular[6] *free-radical dimerization does become important at low chromic acid concentrations and low acidities.*

The dependence on acidity is easily understood in terms of the mechanism given in Scheme I, if one assumes that the oxidation of free radicals (reaction 3) is acid catalyzed, as are almost all known chromium(VI) oxidations, and that the dimerization reaction (reaction 4) is not.

The dependence on the concentration of chromic acid is less obvious, but it can be shown at least semiquantitatively that the observed trend is in agreement with the mechanism of Scheme I.

The two competing reactions which will determine the ratio of the initial rate of chromium(III) formation relative to chromium(VI) reduction are the free-radical dimerization (reaction 4) and free-radical oxidation (reaction 2). The relative rates of the two reactions are given in eq 5.

$$\frac{v_4}{v_2} = \frac{k_4[\cdot CO_2H]}{k_2[Cr(VI)]} \tag{5}$$

Using a steady-state approximation, it can be shown that the concentration of the free-radical intermediate is as shown in eq 6. Dimerization of free radicals (reaction 4)

$$[\cdot CO_2H] = \frac{k_2[Cr(VI)]}{2k_4}\left(\sqrt{1 + \frac{4k_1k_4}{k_2^2[Cr(VI)]}} - 1\right) \tag{6}$$

$$\text{Consequently, } \frac{v_4}{v_2} \doteq \frac{1}{2}\left(\sqrt{1 + \frac{4k_1k_4}{k_2^2[Cr(VI)]}} - 1\right) \tag{7}$$

should become less important relative to their oxidation (reaction 2) as the concentration of chromic acid increases. As more dimerization results in higher values of k_i/k_s, these values should decrease with increasing concentration of chromic acid; this is indeed observed.

According to the mechanism of Scheme I chromium(V) is formed from chromium(VI) and $\cdot CO_2H$. As an increasing fraction of these radicals react by dimerization (reaction 4), the amount of chromium(V) should be reduced. Thus the same factors which increase the values of k_i/k_s should also reduce the amount of chromium(V) formed. The determination of the effect of the concentration of chromic acid and of acidity on the relative amount of chromium(V), formed during the reaction, thus provides an independent check of the above conclusions based on rate studies.

Figure 2 and Table II show that the yield of chromium(V) does indeed depend both on the initial concentration of chromic acid and on the acidity of the solution. The highest concentration of chromium(V) if formed at the highest chromic acid and perchloric acid concentrations, *i.e.*, under conditions which minimize the importance of free-radical dimerization. The lowest concentration of chromium(V) was observed at low chromic acid concentration and low acidity. These results are in full agreement with those of the kinetic study.

Table II
Effect of Reaction Conditions on Maximum Amount of Chromium (V) Formed in the Chromic Acid Oxidation of Oxalic Acid at 25°. Oxalic Acid 0.115 *M*[a]

Cr(VI), 10^3 *M*[b]	$HClO_4$, *M*	$[Cr(V)]_{max}$, 10^3 *M*	$[Cr(V)]_{max}$, %
0.812	0.242	0.132	16.3
	0.388	0.162	19.9
4.06	0.242	0.879	21.7
	0.388	1.00	24.6
8.12	0.242	2.10	25.9
	0.388	2.44	30.0

[a] Total. [b] Initial concentration of chromium(VI).

Experimental Section

Materials. Oxalic acid (Mallinckrodt AR) and sodium dichromate (J. T. Baker, Reagent) were used without further purification. Perchloric acid solutions were prepared from 60% perchloric acid (B & A Reagent).

Kinetic Measurements. The reactions were followed spectrophotometrically using Cary 14 and Cary 15 spectrophotometers equipped with thermostated cell holders. The rates were determined by following the increase in the absorbance of chromium(III) at 600 nm.

Chromium(V). The oxidation of oxalic acid by chromic acid was followed spectrophotometrically at 25° by scanning between 410 and 600 nm at time intervals. For each measurement the concentration of chromium(V) was determined from eq 8, following

$$[Cr(V)] = \frac{1}{\epsilon_5}(A_{410} - \epsilon_3[Cr(III)] - \epsilon_6[Cr(VI)]) \tag{8}$$

essentially Srinivasan's[3] procedure. The concentration of Cr(III) was determined from measurements at 600 nm where Cr(III) is the only absorbing species. The concentration of Cr(VI) was calculated from the expression $[Cr(VI)] = [Cr(VI)]_0e^{-kt}$, where k is the pseudo-first-order rate constant for the reduction of Cr(VI) and was determined separately from measurements at 350 nm. Previously reported values[3] for the extinction coefficients of the chromium species at these wavelengths were used.

Registry No.—Oxalic acid, 144-62-7; chromic acid, 13530-68-2.

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(5) In the limiting case, when $k_4[\cdot CO_2H] \gg k_2[CR(VI)]$, all chromium(VI) should be reduced directly to chromium(III) and, consequently, no chromium(V) formation should be observed.

(6) A bimolecular free radical disproportionation reaction $2\cdot CO_2H \rightarrow CO_2 + HCO_2H$ would fit the results of the kinetic study equally well; however, we were unable to detect any formic acid among the reaction products.

Conformational Analysis. CV. The Syn-Diaxial Methyl/Carboethoxy Interaction[1,2]

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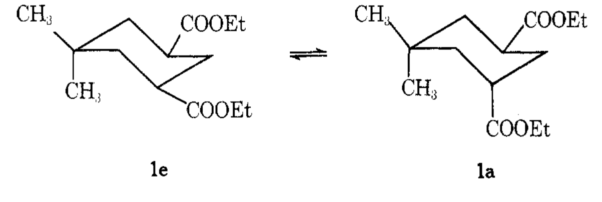
The cis and trans isomers of diethyl 5,5-dimethyl-1,3-cyclohexanedicarboxylate were prepared and equilibrated in alcohol in the presence of ethoxide ion at temperatures ranging from 23 to 102°. For the reaction trans ⇌ cis, the following thermodynamic parameters were determined: $\Delta G° = -2.44$ kcal/mol, $\Delta H° = -2.98 \pm 0.30$ kcal/mol, and $\Delta S° = -1.84 \pm 0.60$ eu. These numbers permit us to assign the syn-diaxial CH_3/COOEt interaction energy as 3.2 kcal/mol.

Because of their simplicity, cyclohexane rings have been an important foundation in conformational studies.[3] The conformational energies of all of the common substituents, and many less common ones, on a cycohexane ring are now pretty well known.[4] Surprisingly, data on systems which contain two syn-axial groups are very sparse. The systems for which data are available seem to be limited to OH/OH ($\Delta G° = 1.9$ kcal/mol[5]), OAc/OAc ($\Delta G° = 2.0$ kcal/mol[6]), CH_3/OH ($\Delta G° = 1.9$–2.4 kcal/mol[7]), CH_3/CH_3 ($\Delta G° = 3.7$ kcal/mol[8]), Cl/Cl ($\Delta G° = 5.5$ kcal/mol[9]), CH_3/Br ($\Delta G° = 2.2$ kcal/mol[10]), CH_3/F ($\Delta G° = 0.37$ kcal/mol[11]), and CH_3/X ($\Delta G° > 1.0$ kcal/mol for X = Cl, Br, and I[11]). The present paper is concerned with a determination of the value for the syn-diaxial CH_3/COOEt interaction.

To measure the interaction in question, the equilibrium between the cis and trans isomers of diethyl 5,5-dimethyl-1,3-cyclohexanedicarboxylate (1) was studied in alcoholic solution in the presence of base at temperatures ranging from 23 to 102°.



1e **1a**

One might question whether or not this equilibrium would measure simply a steric effect. After all, the carboethoxyl groups are polar groups, and they change their relative distance and orientation in the epimerization. The question is not easy to answer theoretically, because the charge distribution in a carboethoxyl group is complicated, and various conformational isomers are possible, which differ by rotations about the ester groups. However, it is known experimentally that the enthalpy of isomerization of diethyl 1,3-cyclohexanedicarboxylate[12] does not differ significantly from that of ethyl carboxylate or from those of the ethyl 4-alkylcarboxylates.[13]

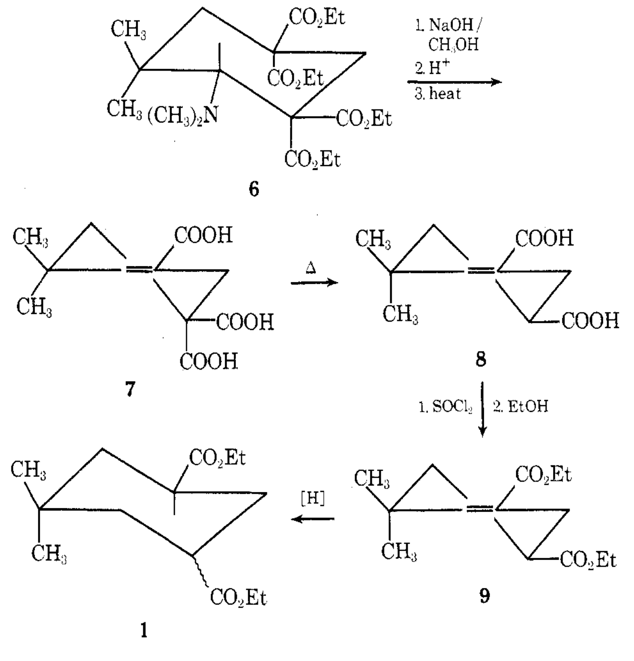
Results and Discussion

Synthesis. Compound **1** presented some unusual synthetic problems, since the axial methyl group obviated many of the usual condensation routes to this type of compound. The synthetic sequence used is shown. The synthesis of **6** by this method has been previously reported[14] and will not be discussed here. Treatment of **6** with base, followed by acidification, rapidly effects a decarboxylative elimination to yield the unsaturated tricarboxylic acid **7**. An examination of Dreiding models points out the great steric crowding which exists in **6**, and the rapid decarboxylative elimination of the tetraacid of **6** probably reflects the large decrease in steric repulsion in the product. An interesting aspect of the unsaturated triacid **7** is its inability to undergo facile hydrogenation at

$$\underset{\textbf{2}}{C_2H_5OCH{=}C(CO_2C_2H_5)_2} \xrightarrow[H_2]{PtO_2}$$

$$\underset{\textbf{3}}{C_2H_5OCH_2CH(CO_2Et)_2} \xrightarrow{\Delta} \underset{\textbf{4}}{CH_2{=}C(CO_2Et)_2}$$

$$\textbf{4} + \underset{\textbf{5}}{(CH_3)_2C{=}CHN(CH_3)_2} \xrightarrow{\Delta}$$



6 **7** **8** **9** **1**