Formation of a Long-Lived Chromium(V) Intermediate in the Chromic Acid Oxidation of Oxalic Acid[1]
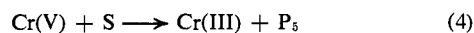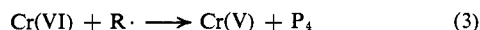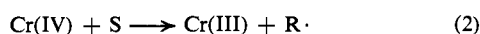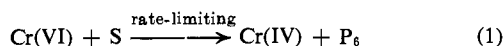
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Abstract: The formation and disappearance of a relatively stable chromium(V) intermediate during the reaction of chromic acid with oxalic acid can be conveniently observed by electron spin resonance as well as by spectrophotometric studies. The esr signals indicate the existence of two chromium(V) species which are in rapid equilibrium and whose relative concentrations depend on the composition of the solvent. Absorption spectra of chromium(V) in 50% acetic acid and water have been constructed. It is shown that chromium(V) resembles chromium(VI) in most of its kinetic properties, and under most conditions is only two to three times more reactive toward oxalic acid.
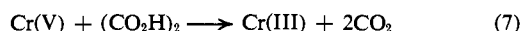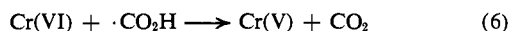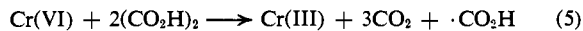
Chromium(V) plays an important role in chromic acid oxidations.[3] According to reaction Scheme I,[4] which has been established for chromic acid oxida-

Scheme I

$$Cr(VI) + S \xrightarrow{\text{rate-limiting}} Cr(IV) + P_6 \qquad (1)$$

$$Cr(IV) + S \longrightarrow Cr(III) + R\cdot \qquad (2)$$

$$Cr(VI) + R\cdot \longrightarrow Cr(V) + P_4 \qquad (3)$$

$$Cr(V) + S \longrightarrow Cr(III) + P_5 \qquad (4)$$

tion of alcohols,[5] aldehydes,[6] and oxalic acid (first-order term),[7] and which is likely to be valid for a number of other chromic acid oxidations, only one-third of the reaction products stems directly from the well-investigated chromium(VI) oxidation, whereas two-thirds of the products are formed in reactions involving unstable chromium(IV) and chromium(V) intermediates. In the main reaction sequence (Scheme II) in the chromic acid

Scheme II

$$Cr(VI) + 2(CO_2H)_2 \longrightarrow Cr(III) + 3CO_2 + \cdot CO_2H \qquad (5)$$

$$Cr(VI) + \cdot CO_2H \longrightarrow Cr(V) + CO_2 \qquad (6)$$

$$Cr(V) + (CO_2H)_2 \longrightarrow Cr(III) + 2CO_2 \qquad (7)$$

oxidation of oxalic acid,[8] chromium(V) oxidation is responsible for 33% of the oxidation products. Chromium(V) oxidations also participate in the oxidation process in the recently discovered cooxidation reactions.[9] Chromium(V) is believed to be responsible for

67% of the reaction products in the chromic acid oxidations of hydrazine,[10] uranium(IV),[11] and other compounds.[12]

Wiberg and Schäfer[13] were able to detect and study the formation of a chromium(V) intermediate in the chromic acid oxidation of isopropyl alcohol in acetic acid solutions. However, the conditions under which the formation of chromium(V) could be observed were limited, and the lifetime of the intermediate was so short as to necessitate the use of fast reaction techniques. The studies could not be extended to aqueous solutions.

In a search for a more convenient source of chromium(V) we became interested in a report by Kon[14] that an esr signal, which could be ascribed to a chromium(V) compound, was observed when chromic acid was reduced by certain substrates, e.g., oxalic, lactic, citric, or malonic acid. A preliminary experiment carried out in our laboratories[15] confirmed these findings and showed further that the chromium(V) intermediate is rather long lived, and can be observed in both acetic acid and aqueous media. This work is devoted to a more detailed investigation of the formation and kinetic behavior of chromium(V) during the oxalic acid oxidation by chromium(VI).

Experimental Section

Stock solutions of chromium trioxide (Mallinckrodt, AR grade), oxalic acid (Baker Analyzed), and perchloric acid (Baker and Adamson) in the appropriate solvent, most frequently 50% (v/v) aqueous acetic acid (Fischer-ACS grade), were prepared. Required aliquots of oxalic and perchloric acid solutions were transferred to a 25-ml flask, made up almost to the mark, and kept in a thermostated bath at 25° for at least 0.5 hr prior to the initiation of a run. A run was initiated by the addition of the required aliquot of chromium trioxide solution, making up to the mark, and transferring to a spectrophotometer cell or an esr liquid sample tube. In the spectrophotometric studies, a Cary Model 14 or 15 recording spectrophotometer fitted with a thermostated cell compartment was used: 1-cm cells were used for runs at 350 nm, 5- or 10-cm cells were required for measurements at 405 and 580 nm. Esr spectra were recorded with a Japan Electron Optics Lab. Co., Ltd. spec-

(1) This investigation was supported by the National Science Foundation.

(2) On leave from the Department of Chemistry, Kurukshetra University, India.

(3) (a) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949); (b) K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965; (c) R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964.

(4) P₆, P₅, and P₄ in this and following reaction schemes indicate oxidation products resulting from the initial interaction of the substrate with chromium(VI), chromium(V), and chromium(IV), respectively.

(5) (a) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); (b) *ibid.*, **95**, 7123 (1973); (c) M. Rahman and J. Roček, *ibid.*, **93**, 5455, 5462 (1971); (d) P. M. Nave and W. J. Trahanovsky, *ibid.*, **92**, 1120 (1970); (e) K. B. Wiberg and S. K. Mukherjee, *ibid.*, **93**, 2593 (1971).

(6) C. S. Ng, Ph.D. Thesis, University of Illinois at Chicago Circle, 1973.

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

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

(9) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181, 8946 (1972); **95**, 5421 (1973); *J. Org. Chem.*, **38**, 3812 (1973).

(10) G. P. Haight, Jr., T. J. Huang, and B. Z. Shakashiri, *J. Inorg. Nucl. Chem.*, **33**, 2169 (1971).

(11) J. H. Espensen and R. T. Wang, *Inorg. Chem.*, **11**, 955 (1972).

(12) K. K. Sen Gupta and J. K. Chaklandar, *J. Chem. Soc., Perkin Trans. 2*, 929 (1973).

(13) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 927 (1969); **89**, 455 (1967).

(14) (a) H. Kon, *Bull. Chem. Soc. Jap.*, **35**, 2054 (1962); (b) *J. Inorg. Nucl. Chem.*, **25**, 933 (1963).

(15) M. Rahman, unpublished results.

Figure 1. Esr spectra of the chromium(V) intermediate in the the chromic acid oxidation of oxalic acid: (a) 50% AcOH; (b) 50% AcOH in Q-band; (c) water; (d) 100% AcOH; (e) 50% AcOH at liquid nitrogen temperature. All measurements except b are in X-band; all measurements except e are at 25°. Concentrations: (d) CrO_3 = 0.00042 M, oxalic acid = 0.019 M. All others: CrO_3 = 0.00081 M, oxalic acid = 0.076 M, $HClO_4$ = 0.024 M.

Table I. g Values and Ratio of Derivative Heights in CrO_3–Oxalic Acid System[a]

Solvent composition, % HOAc (v/v)	g values		Ratio of derivative heights 1st/2nd peak[b]
	First line	Second line	
0	1.976	1.971	0.26
15	1.976	1.971	0.26
30	1.976	1.970	0.31
50	1.977	1.971	0.46
70	1.977	1.971	0.91
80	1.977	1.971	1.53
88	1.977	1.971	2.55
100	1.978	1.973	5.59
50*	1.975	1.964	
88*	1.976	1.963	

[a] Temperature 25°, except asterisked (*) runs, which were measured at liquid nitrogen temperature; concentrations: CrO_3 = 8.07 × 10⁻⁴ M; oxalic acid = 7.6 × 10⁻² M; $HClO_4$ = 0.24 M, except at 100% HOAc, where CrO_3 = 4.16 × 10⁻⁴ M; oxalic acid = 1.86 × 10⁻² M. [b] For greater precision measured at t_{max}, i.e., at the time at which a plot of derivative height vs. time reaches a maximum.

trometer (Model 3BSX) employing 100-kHz field modulation. The cavity and sample tube were kept at 25°; g values were measured by reference to diphenylpicrylhydrazyl (DPPH; g = 2.0036). Field calibration was obtained by reference to the known value of the nitrogen hyperfine coupling in potassium nitrosodisulfonate. In 50% acetic acid the reaction went to completion in 30–120 min, depending on the concentration of the reactants.

Results and Discussion

Esr Studies. Figures 1a–e give examples of esr spectra recorded during the chromic acid oxidation of oxalic acid under a number of conditions. The esr spectra consist of two intense narrow lines. Figure 1e gives the esr spectrum of a frozen solution of chromic acid–oxalic acid mixture in 50% acetic acid. Table I gives the g values obtained for solutions of chromic acid–oxalic acid mixtures under a wide range of conditions. The values at liquid nitrogen temperature compare favorably with the values g = 1.962 and g = 1.978 reported by Kon[14] for frozen solutions of potassium dichromate and oxalic acid in glacial acetic acid. Satellite peaks observed by Kon[14] and ascribed by him to the ⁵³Cr isotope could be observed only on high magnification. The good agreement between the g values suggests that the esr signals observed during the chromium trioxide–oxalic acid reaction under a wide range of conditions are due to the formation of quinquevalent chromium as an intermediate. No esr signals were observed in solutions of chromium trioxide in 50% acetic acid in the absence of oxalic acid.

During the course of a run, the peak to peak derivative height of the two lines first increased with time, reached a maximum, and then decreased until the signals faded away altogether on completion of the reaction. During any one run the derivative heights of the two lines maintained at a constant ratio. The esr spectrum of an oxidation mixture in which all the chromium had been converted into the trivalent state and having a chromium content about 40 times more than that used normally in this study showed a single very broad line spread over about 1000 G, thus ruling out the possibility that the two-line esr spectrum corresponded to a chromium(III) compound. Chromium(IV) is also a paramagnetic reaction intermediate; however, due to the presence of two unpaired electrons, all known chromium(IV) compounds with oxygen ligands produce esr signals only at very low temperatures.[16,17] Thus there is little doubt that the two-line esr spectrum observed by us is due to chromium(V).

At 25° the two lines have a separation of 9.8 G in X-band frequencies and 40 G in Q-band frequencies (Figures 1a and 1b, respectively). This suggests that the two lines are not hyperfine components whose separation should be frequency independent, but that two chromium(V) species are present. The fact that the two lines grow and decay at the same rate further suggests that the two species are in rapid equilibrium which is established faster than their formation. The last column of Table I, which gives the ratio of the derivative heights of the two esr lines at the time when they reach a maximum, shows that the relative concentration[20] of the two species is strongly solvent dependent.[23]

(16) E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chrisholm, J. Chem. Soc. A, 772 (1971).

(17) It was recently reported that tetraalkylchromium(IV) compounds, on the other hand, give esr signals even at room temperature.[18,19]

(18) G. A. Ward, W. Kruse, B. K. Bower, and J. C. W. Chien, J. Organometal. Chem., 42, C43 (1972).

(19) W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, J. Chem. Soc., Dalton Trans., 533 (1972).

(20) The concentration of the paramagnetic species is strictly proportional to the double integral of the first derivative of the esr spectrum. The above integral may be approximated to the product of the peak to peak derivative height and the square of the peak to peak derivative width at half-height.[21,22] Since the same two paramagnetic species are present throughout any one run, and in solutions of different
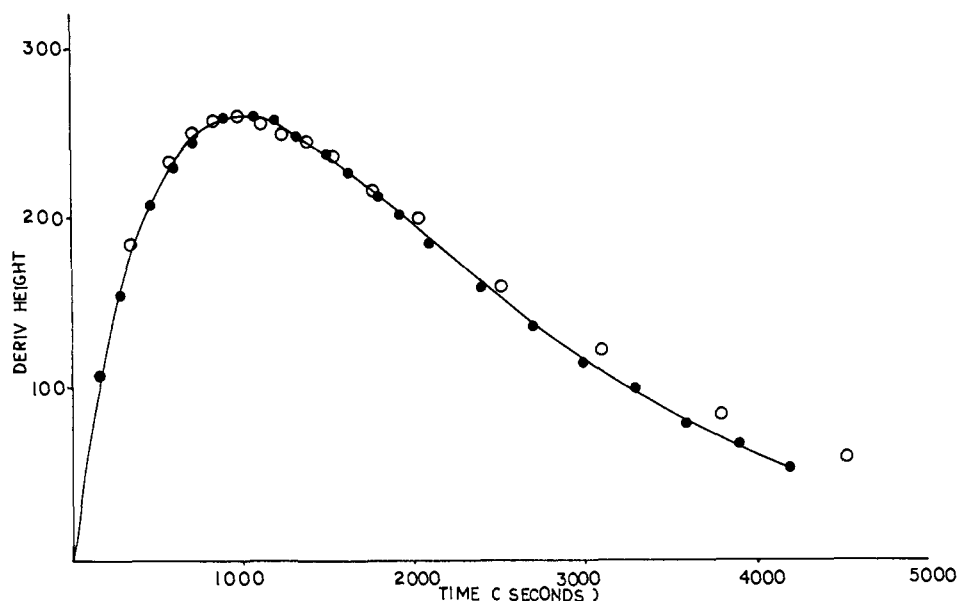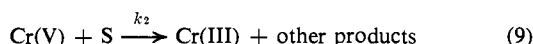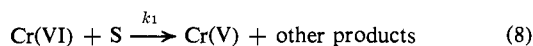
Figure 2. Time dependence of derivative height of the esr signal: (O) experimental points; ($\bullet$) calculated for $k_1 = 0.685 \times 10^{-3}$ sec^{-1}, $k_2 = 1.37 \times 10^{-3}$ sec^{-1}, $CrO_3 = 0.00081\,M$, oxalic acid $= 0.076\,M$, $HClO_4 = 0.24\,M$.

On the other hand, the concentration ratio remained constant even when the concentration of oxalic acid (in 50% acetic acid) was varied over a 100-fold[24] range at constant chromic acid concentration. The two observable chromium(V) species thus differ probably in the nature or degree of coordination with the solvent, but not in the number of oxalic acid molecules associated with the chromium atom.[25] The formation and decay of the chromium(V) intermediate can be observed and measured[20] by following the change in the peak to peak derivative height of the esr signal with time. Figure 2 (open circles) gives a representative sample of such plots. The curve exhibits the typical behavior of an intermediate formed during a sequence of consecutive reactions.

In all runs oxalic acid was at least in 20-fold excess over chromium(VI), ensuring pseudo-first-order conditions. Under this condition, the simplified Scheme III

Scheme III

$$Cr(VI) + S \xrightarrow{k_1} Cr(V) + \text{other products} \qquad (8)$$

$$Cr(V) + S \xrightarrow{k_2} Cr(III) + \text{other products} \qquad (9)$$

given could be used for the quantitative treatment

of the data. The concentrations of the three oxidation states of chromium at time t are then given by

$$A = A_0 e^{-k_1 t} \qquad (10)$$

$$B = \frac{k_1 A_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \text{ (when } B_0 = 0) \qquad (11)$$

$$C = A_0 - A - B \qquad (12)$$

where A, B, and C represent the concentrations of chromium(VI), chromium(V), and chromium(III), respectively, the subscript zero refers to initial concentrations, and k_1 and k_2 are the pseudo-first-order rate constants for the disappearance of chromium(VI) and chromium(V).[28]

Equation 11 gives the concentration of chromium(V) as a function of time. As the value of k_1 can be obtained from spectrophotometric studies (see below), the chromium(V) concentration could be calculated as a function of time for different assumed values of k_2. The computer calculated curves and the experimental curves derived from esr derivative heights were normalized at the point of maximum concentration and then compared. The k_2 values that gave the best fit between the two curves were selected. Figure 2 gives a comparison of experimental (open circles) and calculated (closed circles) data under one set of conditions. The very good fit of the experimental and calculated points supports reaction Scheme II, from which eq 11 was derived. By this procedure, optimum values of k_2 were obtained over a range of reaction conditions.

Spectrophotometric Studies. In order to calculate the concentration of chromium(V) according to eq 8, we needed the rate constant k_1 for the disappearance of chromium(VI). When we tried to determine its value, using the standard procedure of plotting log (Abs) vs. time at 350 nm, we obtained a curve (Figure 3), which turned into the expected straight line only after a period of time which was approximately equal to the time re-

solvent composition, the derivative width remained constant, both with changes in solvent composition and with time. It was therefore possible to use peak to peak derivative heights as measures of relative concentrations both in the study of solvent affects and particularly in the kinetic situation of the formation and decay of the chromium(V) species.

(21) R. S. Ager, "Electron Paramagnetic Resonance," Interscience, New York, N. Y., 1968, p 200.
(22) R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960).
(23) Dr. George F. Vandegrift in this laboratory noted that only a single signal is observed if a small amount of acetic anhydride is added to a sample in glacial acetic acid.
(24) We wish to thank Dr. George F. Vandegrift for carrying out this part of the study.
(25) Mishra and Symons[26] observed the appearance of two intense lines of variable intensities for chromium(V) in the range of 100% sulfuric acid to 30% oleum, but not in 65% oleum, and Garif'yanov[27] observed a similar effect in dimethylformamide but not in acetone.
(26) H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4490 (1963).
(27) S. Garif'yanov, A. V. Il'yasov, B. M. Kozyrev, and Z. I. Usmanov, *Dokl. Akad. Nauk SSSR*, **198**, 868 (1971).

(28) Throughout the discussion it is assumed that chromium(IV) is present only in negligibly low concentrations. This assumption is justified by its very high oxidative power.[5–7]
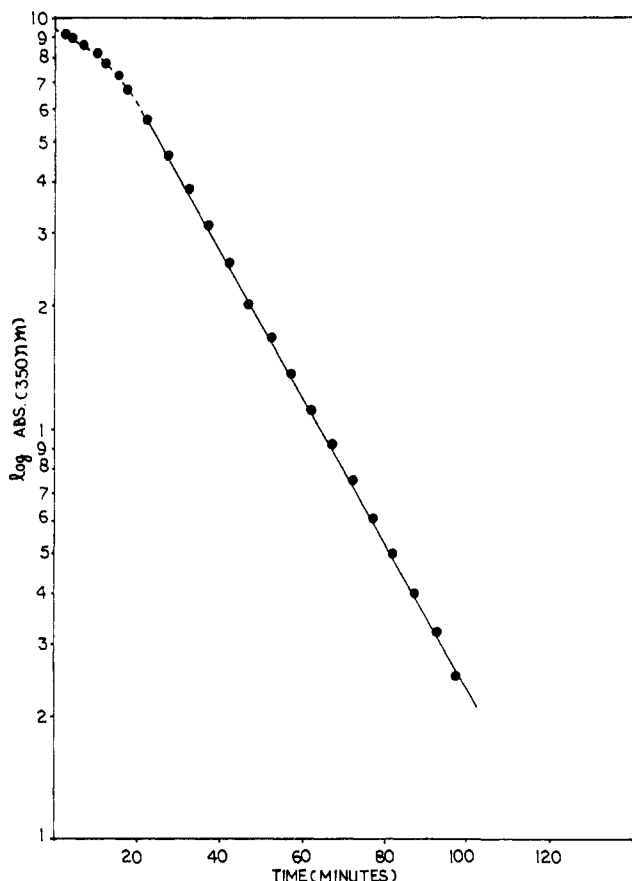
Figure 3. Time dependence of log Abs at 350 nm; conditions as in Figure 2.

quired to reach the maximum in the derivative height *vs.* time plot in the esr experiment under identical conditions. Although the appearance of the curve at first inspection suggested the existence of an induction period, a more probable explanation seemed to be that the chromium(V) intermediate absorbed sufficiently strongly at 350 nm to compensate for the decrease in absorbance due to the reduction of chromium(VI). This observation prompted us to investigate the possibility that the formation of the intermediate could be followed also spectrophotometrically.

Figure 4 shows the difference between the visible absorption spectrum of an oxidation mixture recorded at three time intervals in the course of the reaction and the spectrum of chromium(VI) at the same initial concentration. The initial increase of the absorption at 405 nm indicates the formation of an intermediate absorbing strongly in the vicinity of 405 nm and whose formation and disappearance occur at a measurable rate.

The total absorbance of the system at any wavelength is given by

$$\text{Abs} = l(\epsilon_a A + \epsilon_b B + \epsilon_c C) \tag{13}$$

where l is the length of the light path and ϵ_a, ϵ_b, ϵ_c are the molar absorptivities of chromium(VI), chromium(V), and chromium(III), respectively. When applied to the absorbance at 405 nm, where all the three chromium species absorb, $\epsilon_b Bl$, which is the absorbance of chromium(V), is given by

$$\epsilon_b Bl = \text{Abs (at 405 nm)} - \epsilon_a Al - \epsilon_c Cl \tag{14}$$

The quantity $\epsilon_a Al$, which is the absorbance of chromium(VI) at 405 nm, can be calculated from eq 15, using

$$\epsilon_a Al = \text{Abs (at 350 nm)} \times (\epsilon_a l / \epsilon_a' l') \tag{15}$$

experimental values of absorbance at 350 nm under the same concentration conditions. Here ϵ_a' and l' are the molar absorbtivities of chromium(VI) at 350 nm and the length of the light path used at this wavelength. The quantity $\epsilon_a l / \epsilon_a' l'$ is a constant factor and is calculated independently. The value of $\epsilon_c Cl$ can be calculated similarly from measurements at 580 nm, the absorption maximum for chromium(III).[29]

Figure 5 (open circles) gives a representative example of a curve that shows the formation and decay of the intermediate determined spectrophotometrically at 405 nm in the manner described above. Using the same procedure as described in the esr section, the experimental curve was compared with calculated curves, giving concentration of chromium(V) as a function of time, and the best fitting value of k_2 was selected. The conditions used in the esr measurements in Figure 2 and in the spectrophotometric measurements in Figure 5 are identical. Further, the same values of k_1 and k_2 were used to construct the calculated curve in the two figures. The fact that two independent experimental methods yielded identical values for k_2 confirms the assumption that the same intermediate was observed in esr and spectrophotometric studies. Repeating the procedure for a number of reaction conditions, we found that the k_2 values obtained from esr measurements were confirmed by spectrophotometric studies.

The total absorbance of the system at any wavelength is given by eq 16, which is readily derived from eq 10–13.

$$\text{Abs} = lA_0\left[(\epsilon_a - \epsilon_c) e^{-k_1 t} + \frac{k_1}{k_2 - k_1}(\epsilon_b - \epsilon_c)(e^{-k_1 t} - e^{-k_2 t}) + \epsilon_c\right] \tag{16}$$

The molar extinction coefficient of chromium(III), ϵ_c, is small enough at 350 nm (4.3 mol^{-1} cm^{-1}) to be ignored. Hence, at 350 nm eq 14 will be reduced to eq 17.

$$\text{Abs} = l\left[\epsilon_a A_0 e^{-k_1 t} + \epsilon_b A_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})\right] \tag{17}$$

The term $e^{-k_2 t}$ becomes small in comparison with $e^{-k_1 t}$ during the later phase of the reaction, when t becomes large, if k_2 is greater than k_1. Equation 17 then further simplifies to eq 18 and 19[30] where $K = l[\epsilon_a + \epsilon_b k_1/$

(29) The calculation of absorbance due to chromium(V) from eq 14 suffers from a certain error. The treatment outlined above ignored the fact that the absorption of chromium(V) at 350 nm is not negligible; consequently the correction for the chromium(VI) absorption at 405 nm calculated from eq 15 is somewhat too high and the actual value of $\epsilon_b Bl$ will be slightly higher than calculated. However, the error is only minor as the absorption of chromium(VI) at 405 is quite low and further as the concentration of the intermediate remains relatively low compared with the total chromium concentration (under most favorable conditions less then 15% of the total chromium is present as chromium-(V) at the time when its absorbance *vs.* time plot reaches its maximum).

(30) Using a simple computer program based on eq 17, it can be shown that curves of the type represented by Figure 3 will indeed result.[31] To make the actual curve given in Figure 3, the following values gave the best fit: $k_1 = 0.34 \times 10^{-3}$ sec^{-1}; $k_2 = 1.0 \times 10^{-3}$ sec^{-1}; $A_0 = 8.1 \times 10^{-4}$ M; ϵ_a 1080 mol^{-1} cm^{-1}; and ϵ_b 1520 mol^{-1} cm^{-1}. It will be noticed that the k_2 value used here is higher than the one used in the construction of the calculated curve in Figures 2 and 5, but that it lies well within the general range of k_2 values reported by us in Tables II and III (see below).

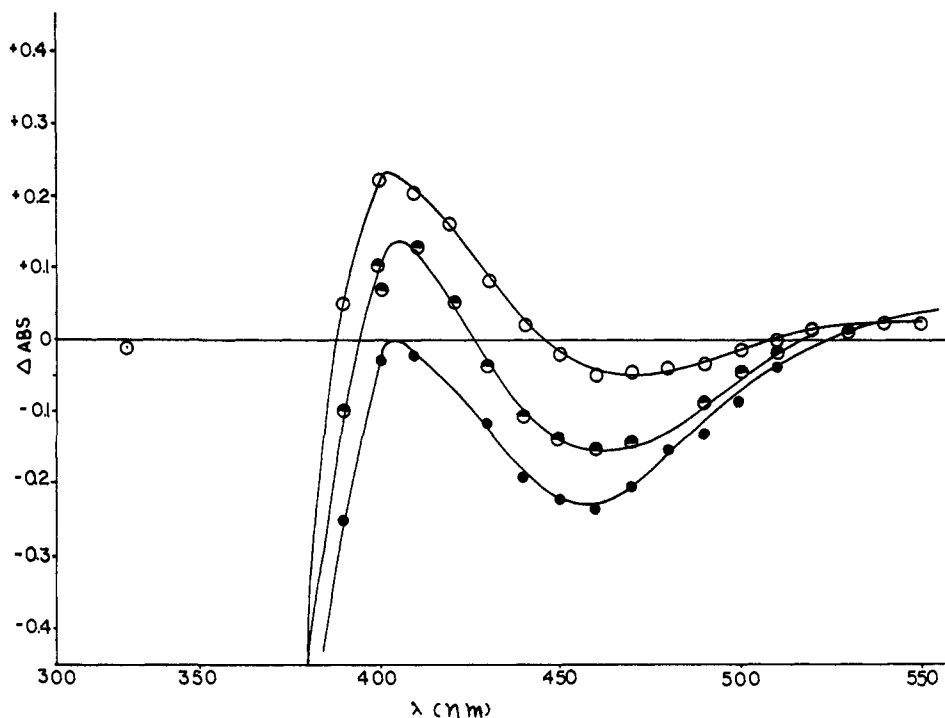(31) We wish to thank Mr. Martin Roček for these computer calculations.

Figure 4. Difference spectrum in the chromic acid oxidation of oxalic acid. Abs = Abs(obsd) − Abs(Cr(VI)) where Abs(Cr(VI)) = Abs of a solution of CrO_3 of identical initial concentration as in the oxidation mixture. Solvent and reference, 50% AcOH: (O) 15 min, (◐) 24 min, (●) 29 min after mixing. Conditions: CrO_3 = 0.00081 M, oxalic acid = 0.038 M, $HClO_4$ = 0.24 M.
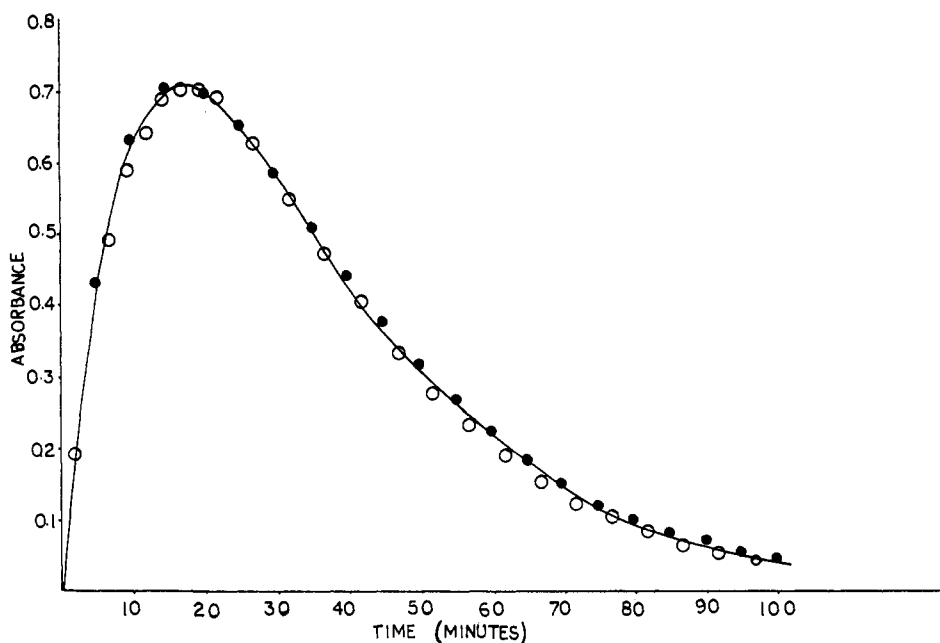

Figure 5. Time dependence of absorbance of intermediate at 405 nm. Abs = $\epsilon_b Bl$, (O) experimental points, (●) concentration of Cr(V) calculated for same k_1 and k_2 as in Figure 2. All concentrations same as in Figure 2.

$(k_2 - k_1)]$.

$$\text{Abs} = KA_0 e^{-k\,t} \qquad (18)$$

$$\log(\text{Abs}) = \log KA_0 - 0.4342 k_1 t \qquad (19)$$

Equation 19 has the linear form expected for first-order reactions, and is valid for absorbance measurements at 350 nm in the later part of the reaction. Thus, the pseudo-first-order rate constant, k_1, for the disappearance of chromium(VI) (reaction 5) could be determined from the linear part of log (Abs) vs. time plots at 350 nm.[32]

An iterative computer program, which could mini-

(32) The experimental pseudo-first-order rate constants obtained from the linear part of the log (Abs) vs. time plot corresponds to the rate of reduction of chromium(VI). According to the reaction mechanism given in Scheme II, the rate of formation of chromium(V) is one-half of this value. If the possibility of a bimolecular reaction[5c,33,34] of the free-radical intermediates is taken into account, then the rate constant for the formation of chromium(V) would be even lower than $k_{exp}/2$. However, these considerations were ignored in the calculations in this work, and the k_{exp} values were used for k_1 without corrections. It can be shown that using $k_{exp}/2$ instead of k_{exp} for k_1 would lead to k_2 values of about one-half of the values given in the tables, but would have little effect on the k_1/k_2 ratios.

(33) K. Meyer and J. Roček, *J. Amer. Chem. Soc.*, **94**, 1209 (1972).
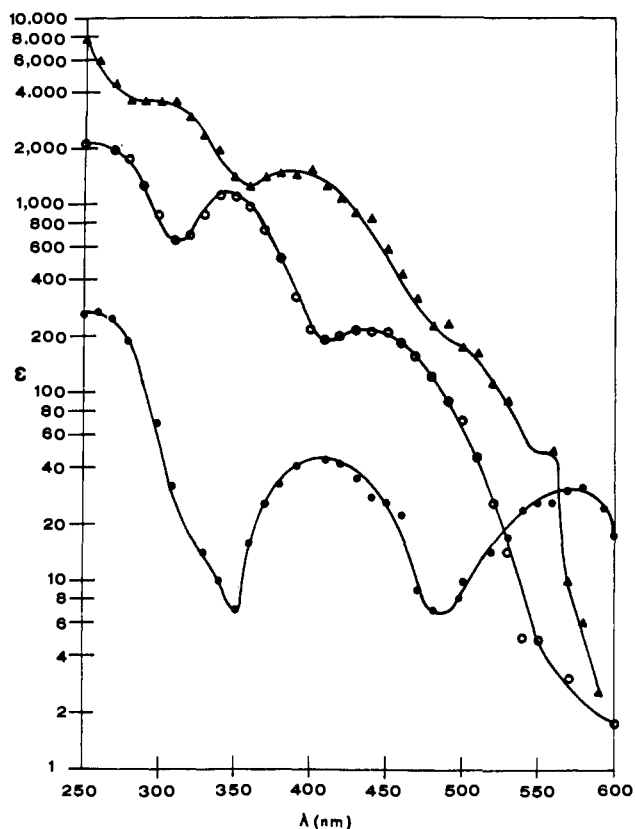(34) F. Hasan and J. Roček, *ibid.*, in press.

Figure 6. Spectra of chromium(VI), chromium(V), and chromium(III) in 50% acetic acid (v/v = 51.2% w/w): (O) chromium(VI), (△) chromium(V), and (●) chromium(III).
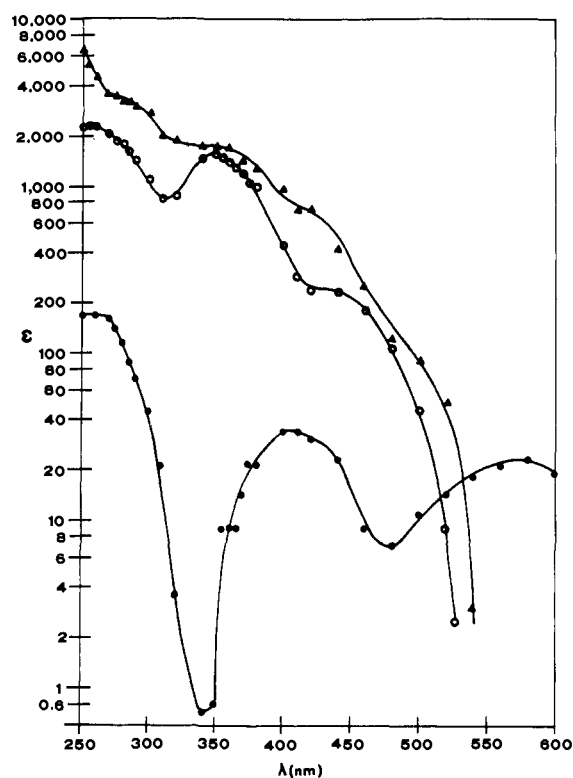

Figure 7. Spectra of chromium(VI), chromium(V), and chromium(III) in water: (O) chromium(VI), (△) chromium(V), and (●) chromium(III).

Table II. Pseudo-First-Order Rate Constants for Disappearance of Chromium(VI) (k_1) and Chromium(V) (k_2) in Chromic Acid Oxidation of Oxalic Acid[a]

[CrO₃] × 10^4, M	[Oxalic Acid] × 10^2 M	[HClO₄], M	$10^3 k_1$, sec⁻¹	$10^3 k_2$, sec⁻¹	k_2/k_1
8.073	2.06	0.24	0.089	1.42	16.0
8.073	3.80	0.24	0.26	1.18	4.5
8.073	7.60	0.24	0.75	1.44	1.9
8.073	11.40	0.24	1.20	3.54	3.0
8.073	15.20	0.24	1.81	5.45	3.0
8.073	19.00	0.24	2.84	8.17	2.9
8.073	20.83	0.24	3.18	9.46	3.0
8.073	11.40	0.0	1.60	3.12	1.9
8.073	11.40	0.122	1.34	3.30	2.5
8.073	11.40	0.183	1.61	3.64	3.0
8.073	11.40	0.24	1.20	3.54	2.9
8.073	11.40	0.305	1.16	3.44	3.0
8.073	11.40	0.651	0.97	3.36	3.5
8.073	11.40	1.302	0.75	3.34	4.5
8.073	11.40	1.952	0.55	3.28	5.9
3.229	11.40	0.122	1.43	3.50	2.5
6.458	11.40	0.122	1.33	3.30	2.5
8.073	11.40	0.122	1.36	3.30	2.5
11.73	11.40	0.122	1.32	3.30	2.5

[a] Solvent = 50% aqueous acetic acid, temperature = 25°.

Table III. Influence of Solvent Composition on Rates of Disappearance of Chromium(VI) (k_1) and Chromium(V) (k_2) in Chromic Acid Oxidation of Oxalic Acid[a]

Solvent % HOAc	$10^3 k_1$, sec⁻¹	$10^3 k_2$, sec⁻¹	k_2/k_1
0	0.81	2.44	3.0
15	0.81	2.02	2.5
30	0.75	1.69	2.2
50	0.75	1.43	1.9
70	0.49	1.10	2.2
80	0.35	1.05	3.0

[a] CrO₃ = 8.073×10^{-4} M, oxalic acid = 7.6×10^{-2} M, HClO₄ = 0.24 M, temperature = 25°.

mize the deviation as defined by eq 20, was used to

$$\text{Dev} = \sum_1^n [(\text{Abs(calcd)} - \text{Abs(obsd)}] \quad (20)$$

determine optimal values for ϵ_b, k_1, and k_2. Here n is the number of experimental points fed into the program, Abs(calcd) is the absorbance calculated by eq 16, and Abs(obsd) is the observed absorbance at any wave-

length. This permitted the computation of the molar extinction coefficients of the chromium(V) intermediate at several wavelengths and the construction of absorption spectra (Figures 6 and 7)[35,36]

Table II summarizes the results for k_1 and k_2 obtained with the above computer program for a number of measurements over a fairly wide range of conditions. It is quite obvious that despite some minor fluctuations and a slight increase in the k_2/k_1 ratio with increasing acidity and at low oxalic acid concentrations, chromium(V) and chromium(VI) exhibit a remarkable degree of similarity over the whole range. Table III shows that the change from purely aqueous solution to 80% acetic acid solution has practically no effect on the relative
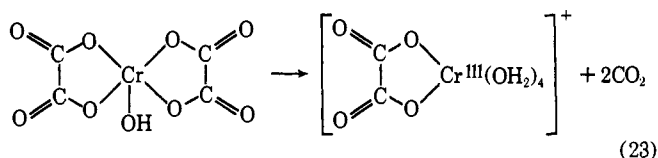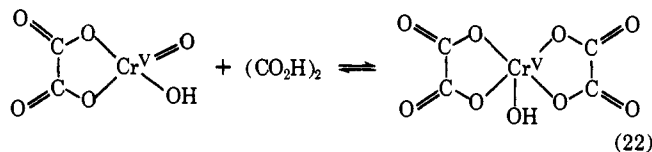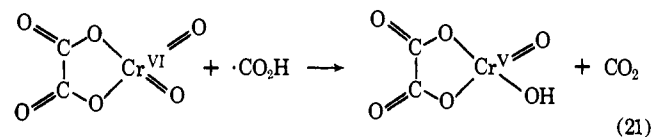
(35) We express our appreciation to Dr. Fariza Hasan for extending our original measurements into the ultraviolet region and into aqueous solutions.

(36) Spectra of several other chromium(V) compounds have been reported in the literature.[14,37,38]

(37) H. L. Krauss, M. Leder, and G. Münster, Chem. Ber., 96, 3008 (1963).

(38) N. Bailey and M. C. R. Symons, J. Chem. Soc., 203 (1957).

Scheme IV

$$(21)$$

$$(22)$$

$$(23)$$

reactivity of chromium(V) to chromium(VI) with respect to oxalic acid.

The independence of the ratio of k_2/k_1 indicates that the oxidation of oxalic acid by both chromium(VI) and chromium(V) follows the same kinetic dependence on the oxalic acid and hydrogen ion concentration. As the oxidation of oxalic acid within the region studied in this work is second order in oxalic acid,[8] it follows that the same order can be assumed for the chromium(V) oxidation, which leads to the conclusion that the chromium-

(V) oxidation of oxalic acid proceeds through a dioxylato complex of chromium(V). This conclusion is in full agreement with earlier observations that around 50% of chromium(III) produced during the reaction contains oxalic ligands.[8,10] The main reaction involving chromium(V) and taking place during the chromic acid oxidation of oxalic acid can be tentatively summarized in Scheme IV.

The results of our study thus indicate that the monooxalato complex of chromium(V) is relatively stable and is responsible for the accumulation of chromium(V) during the chromic acid oxidation of oxalic acid. Further reduction of chromium(V) to chromium(III) seems to occur only after a second molecule of oxalic acid enters the complex.

Fenton's Reagent. IV. Structure and Reactivity Relations in the Reactions of Hydroxyl Radicals and the Redox Reactions of Radicals[1]

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Abstract: Reactivities of a variety of alcohols, ethers, and amides toward hydroxyl radicals have been examined. Results are in encouraging agreement with radiation chemistry results. Reactivities of different C–H bonds have been dissected from the data and indicate that the hydroxyl radical is a strongly electrophilic species, so that electron supply is more important than C–H bond strength in determining reactivity. Comparison with gas-phase data shows similar reactivity patterns, but considerably faster reactions in H_2O. Radicals α to –OH, –OR, and amide N are readily oxidized by Fe^{3+}; *tert*-alkyl radicals are oxidized with more difficulty and allyl radicals hardly at all. In contrast, radicals $R\dot{C}(OH)CCl_3$ are reduced by Fe^{2+}. Results are consistent with a fast oxidation of easily oxidized radicals by Fe^{3+} *via* electron transfer, and a slower more general oxidation of radicals by Cu^{2+} *via* a RCu(III) intermediate.

In a series of recent papers[2,3] we have described a reexamination of the reaction of Fenton's reagent, $Fe^{2+}-H_2O_2$, with a variety of organic substrates. This paper reports results with some additional substrates and summarizes our conclusions, comparing our results with hydroxyl radical reactivity data obtained

from radiation chemistry, and data on the oxidation and reduction of radicals by metal ions (Cu^{2+}, Fe^{3+}, and Fe^{2+}) obtained by other techniques.

The basis of our approach is that, if H_2O_2 is added to an aqueous system containing an organic substrate and excess Fe^{2+} at pH 0–2, the hydroxyl radicals generated attack the substrate and the subsequent course of the reaction and stoichiometry (moles of Fe^{2+} oxidized/mole of H_2O_2 added, $\Delta[Fe^{2+}]/\Delta[H_2O_2]$) depend upon the fate of the organic radicals so pro-

(1) Support of this work by a grant from the National Science Foundation is gratefully acknowledged (Grants No. GP36620X and GP-24300).
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(3) C. Walling and G. M. El-Taliawi, *ibid.*, **95**, 844, 848 (1973).