ties reported.[7] An nmr spectrum (DMSO) with sodium 3-(trimethylsilyl)propanesulfonate as an internal standard showed δ 6.84 (d, 2, J = 3.6 Hz), 7.35 (t, 1, J = 3.6 Hz), and 8.85 ppm (s, 2).

2-Methyl-2H-cyclopenta[*d*]pyridazine (5). Method A. A mixture of 1.29 g (8.66 mmol) of 2-formyl-6-dimethylaminofulvene (**9**),[7] 0.45 ml (14 mmol) of methylhydrazine, and 15 ml of absolute ethanol was swirled to effect solution and then allowed to stand at room temperature. A yellow precipitate formed (10 min) and after 8 hr the collected precipitate together with the residue from the filtrate (solvent removal under reduced pressure with a rotary evaporator) was sublimed twice at 45° (*ca.* 10^{-5} mm) giving 0.93 g (85%) of **5** as a yellow solid: mp 128.8–129.0°; uv max (anhydrous ether) 248 (29,400), 253 (28,900), 268 (15,400), 307 (sh, 12,200), 312 (3810), 317 (3610), 324 (3310), and 395 mμ (ε 821); nmr (CH_2Cl_2) δ 3.95 (s, 3), 6.78 (d, 2, J = 3.4 Hz), 7.38 (t, 1, J = 3.4 Hz), 8.28 (poorly resolved t, 1, J = 0.8 Hz), and 8.67 ppm (broad s, 1). The ir ($HCCl_3$) was recorded.

Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.28; H, 6.42; N, 21.12.

Method B. To 150 ml of methanol (freshly distilled from magnesium methoxide) in a 500-ml, three-necked flask containing 0.415 g (7.69 mmol) of sodium methoxide under dry nitrogen was added 0.5 ml (6.05 mmol) of freshly cracked cyclopentadiene and, after 10 min, 0.949 g (4.16 mmol) of vacuum-dried N-methyl-1,3,4-thiadiazolium iodide (**10**). The color of the solution became golden. The mixture was refluxed for 1.5 hr and then steam distilled (Eastman condenser) for 1 hr. The yellow distillate was extracted with dichloromethane until the extracts were colorless. The residue left after removal of the solvent from the combined, dried ($MgSO_4$) extracts was extracted with boiling heptane. Evaporation of the heptane solution and sublimation (45° (*ca.* 10^{-5} mm)) gave 47.7 mg (8.7%) of **5**, mp 129–130°, identical (uv, ir) with the product from A.

Method C. A mixture of 1.8 g (11.9 mmol) of **9**,[7] 0.58 ml (11.7 mmol) of hydrazine hydrate, and 30 ml of absolute ethanol was refluxed under nitrogen for 2.25 hr, allowed to cool, and was then treated in order with 1.7 ml of 25% sodium hydroxide and 2 ml of methyl iodide. After 4 hr, the solvent was removed (rotary evaporator, aspirator) and the residue was extracted several times with ether under reflux (1 hr). The residue from the combined ether extracts was extracted with several 150-ml portions of *n*-hexane under reflux (1 hr). Sublimation (45° (*ca.* 10^{-5} mm)) of the residue from the *n*-hexane solutions gave 428 mg (27%) of **5** identical (melting point, uv, ir) with the product from A.

2-Phenyl-2H-cyclopenta[*d*]pyridazine (6). The crude product, prepared as described by Hafner, *et al.*,[7] was chromatographed on a short silica gel column with dichloromethane as the eluent. The material obtained was crystallized from absolute ethanol and then sublimed to give **6** as a yellow solid: mp 167–168° (lit.[7] mp 161–162°); uv max (anhydrous ether) 248 (22,400), 258 (sh, 19,800), 287 (28,400), 318 (sh, 7330), and 408 mμ (ε 2850); nmr (CH_2Cl_2) δ 6.83 (pair of doublets, J = 4 Hz, subsplit into triplets, J = 1 Hz, 1), 7.36–7.92 (m, 6), and 8.88 ppm (m, 2).

N-Methyl-1,3,4-thiadiazolium Iodide (10). The red solution formed when a mixture of 3.09 g (36 mmol) of 1,3,4-thiadiazole,[19] 2.5 ml of methyl iodide, and 30 ml of dry dimethylformamide was heated on a steam cone under reflux for 45 min was poured into a beaker and 400 ml of dry ether was added. After filtration, the collected precipitate was washed with ether and vacuum dried (removing an odoriferous impurity) giving 6.67 g (81.5%) of **10** as a light yellow solid, mp 230° dec (lit.[20] 241°), which was used without further purification.

pK_a of 2-Methyl-2H-cyclopenta[*d*]pyridazine (5). A 1.40 × 10^{-3} M stock solution of **5** was prepared by vigorous stirring of 18.5 mg of **5** in 100 ml of distilled water for 3 hr. Individual test solutions were prepared by diluting 10-ml aliquots to 25 ml (5.6 × 10^{-4} M in **5**) with hydrochloric acid of different concentrations such that different solutions having pHs of 1.50–2.72 were obtained as determined on a calibrated (pH 4.01 with phthalate buffer) Beckman Research pH meter at 24–25°. The method used for the pK_a determinations was that described by Albert and Serjeant.[18] Optical densities at 380 mμ were read at 25.0 ± 0.1° on a Beckman Model DU spectrophotometer fitted with a Gifford Absorbance Indicator Model 2000. Maximum slit widths were 0.14 mm. The value of d_m[18] was determined in aqueous sodium formate solution at pH 7.38 and d_i[18] was determined in *ca.* 7.2 N hydrochloric acid. The six pK_a values obtained ranged from 1.92 to 1.98 and the average was 1.95.

---

(19) K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1124 (1961).

(20) J. Goerdeler, J. Ohm, and O. Tegtmeyer, *Ber.*, **89**, 1534 (1957)

Chromic Acid Oxidation of Isopropyl Alcohol. Preoxidation Equilibria[1a]

Kenneth B. Wiberg and Hans Schäfer[1b]

Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06520. Received July 31, 1968

Abstract: The rate and equilibrium constants for the rapid reaction of chromium(VI) with isopropyl alcohol in 97% acetic acid to give the mono- and diesters have been determined by following the change in absorbance with time. The ionization constant of acetochromic acid and the monomer–dimer equilibrium constant for chromium(VI) also have been determined. The results are compared with those for the reaction of *t*-butyl alcohol.

The chromic acid oxidation of alcohols has been examined by many workers.[2] However, the details of the sequence of steps are still not well understood. As a result of the work of Westheimer and his co-workers,[3] it is known that a chromium(VI) ester is an intermediate in the reaction, that carbon–hydrogen bond cleavage is rate determining, and that chromium(IV) is the product of the first step of the reaction. The induced oxidation experiments of Watanabe and West-

---

(1) (a) This investigation was supported by the National Science Foundation. (b) Organic Chemistry Institute, University of Göttingen.

(2) The subject has been reviewed by K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 69 ff.

(3) F. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); F. Westheimer and N. Nicolaides, *J. Am. Chem. Soc.*, **71**, 25 (1949); W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949); J. Roček, F. H. Westheimer, A. Eschenmoser, L. Moldoványi, and J. Schreiber, *Helv. Chim. Acta*, **45**, 2554 (1962).

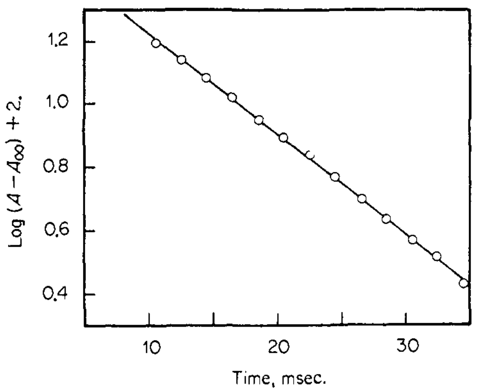


Figure 1. First-order plot for the reaction of isopropyl alcohol with chromic acid in 97% acetic acid; $[CrO_3] = 1.03 \times 10^{-3}\ M$, $[ROH] = 0.046\ M$, $[H^+] = 0.0125\ M$, $T = 15°$.

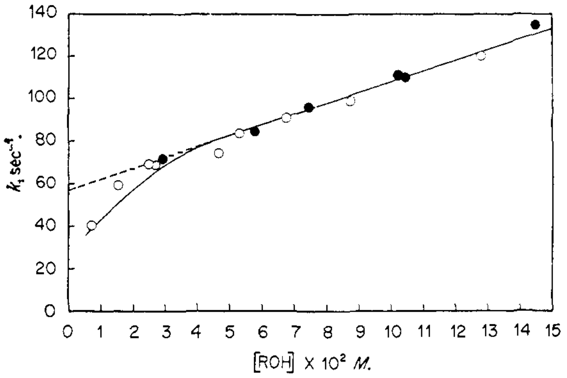


Figure 2. Effect of isopropyl alcohol concentration on the pseudo-first-order rate constants for the reaction with chromic acid, $[H^+] = 0.0125\ M$, 97% acetic acid. The line represents the calculated rate constants: ○, isopropyl alcohol; ●, isopropyl-α-*d* alcohol.

heimer were interpreted to indicate that chromium(V) is formed in one of the steps in the reaction sequence and that it is an active oxidant for the conversion of isopropyl alcohol to acetone. One possible set of reactions was

$$R_2CHOH + HCrO_4^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H \xrightarrow{k_2} R_2C{=}O + Cr^{4+}$$

$$Cr^{4+} + Cr^{6+} \xrightarrow{k_3} 2Cr^{5+}$$

$$2(R_2CHOH + Cr^{5+} \xrightarrow{k_4} R_2C{=}O + Cr^{3+})$$

They also suggested the following scheme.

$$R_2CHOH + HCrO_4 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H \xrightarrow{k_2} R_2C{=}O + Cr^{4+}$$

$$R_2CHOH + Cr^{4+} \xrightarrow{k_3} R_2\dot{C}OH + Cr^{3+} + H^+$$

$$R_2\dot{C}OH + Cr^{6+} \xrightarrow{k_4} R_2C{=}O + Cr^{5+} + H^+$$

$$R_2COH + Cr^{5+} \xrightarrow{k_5} R_2C{=}O + Cr^{3+}$$

The first sequence has subsequently been favored by Westheimer and his coworkers. Recently, Roček[4] has presented evidence indicating that in at least one case the second sequence, involving chromium(IV) as an active oxidant, may be operative.

Regardless of which scheme is correct, it is clear that most of the oxidation of the organic substrate is effected by one of the intermediate chromium species rather than by chromium(VI). For this reason, it seemed important to obtain direct evidence concerning the oxidation by chromium(V) and/or chromium(IV). We have previously indicated that we are able to observe a set of successive reactions spectrophotometrically in 97% acetic acid.[5] This paper will present the details in the preoxidation steps, and the following papers will consider the oxidation steps, the effect of substituents, and also the corresponding oxidation of aromatic aldehydes.

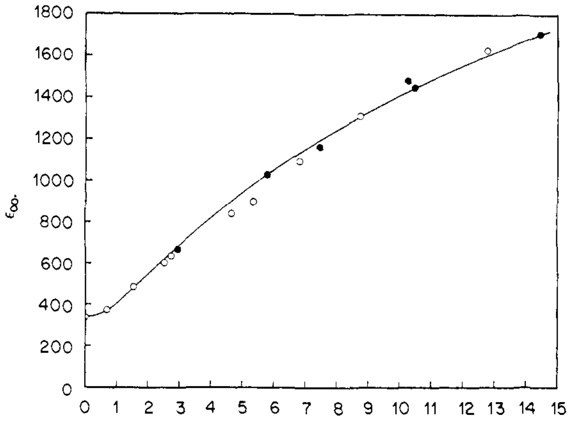


Figure 3. Equilibrium absorbancy indices as a function of isopropyl alcohol concentration. The solid line represents the calculated values ($[H^+] = 0.0125\ M$, 15°, 385 mμ).

The kinetics of the reaction of isopropyl alcohol with chromic acid in 97% acetic acid solution was studied at 385 mμ using a stopped-flow reactor.[6] With a 10–150-fold excess of alcohol and perchloric acid, good first-order plots were obtained (Figure 1). Thus, the reaction has a first-order dependence on the chromic acid concentration. The effect of alcohol concentration on the rate of reaction and on the infinity absorbancy index is shown in Table I. The data are plotted in Figures 2 and 3. The rate constants and infinity absorbance values were calculated using the method of least squares and minimizing errors with respect to variations in the infinity absorbance. This procedure was necessary since a stable infinity value was not obtained as a result of the slower oxidation reaction which followed the initial rapid step. A set of 10–12 runs was made for each set of concentrations and the individual rate constants and infinity values were averaged.

---

[4] J. Roček and E. A. Radkowsky, *J. Am. Chem. Soc.*, **90**, 2986 (1968).

[5] K. B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, **89**, 455 (1967).

[6] J. M. Sturtevant in "Rapid Mixing and Sampling Techniques in Biochemistry," Academic Press, New York, N. Y., 1964, p 89. We are indebted to Professor Sturtevant for the use of his stopped-flow apparatus.

The greatest deviations of the individual rate constants from the average were normally ±7%, and those for the infinity values were less than ±1%.

Table I. Rate Constants and Infinity Absorbancy Indices in the Chromic Acid Oxidation of Isopropyl Alcohol[a]

[alcohol] × 10^2 *M*	*k*, sec^{-1}	$A_\infty/[CrO_3]$
0.7	40.3	379
1.59	59.8	491
2.52	69.3	602
2.71	68.3	634
2.95[b]	71.7	665
4.63	73.6	839
5.30	83.8	896
5.77[b]	84.2	1026
6.7	90.7	1090
7.45[b]	96.1	1161
8.72	98.3	1310
10.45[b]	110.0	1436
10.27[b]	111.0	1479
12.78	120.0	1627
14.45[b]	136.0	1690
10.58[c]	1.52	1632
14.25[c]	1.90	1850
4.6[d]	91.1	915

[a] $[CrO_3] = 1.03 \times 10^{-3}$ *M*, $[H^+] = 1.25 \times 10^{-2}$ *M*, $\mu = 0.183$ *M* ($NaClO_4$), 15.0 ± 0.2°. [b] Isopropyl-α-*d* alcohol. [c] *t*-Butyl alcohol. [d] α-Phenethyl alcohol.

It is important to note that isopropyl-α-*d* alcohol gave the same rate constants and infinity values as the unlabeled alcohol. It is interesting that *t*-butyl alcohol gives infinity values similar to those with isopropyl alcohol, but reacts only $^1/_{70}$ as rapidly.

The effect of acid concentration on the rate of reaction is shown in Table II, and the infinity absorbancy indices are plotted in Figure 4.

Table II. Effect of Acid Concentration on the Rate Constants and Infinity Absorbancy Indices[a]

$[H^+] \times 10^2$ *M*	*k*, sec^{-1}	$A_\infty/[CrO_3]$
	[Alcohol] = 0.0301 *M*	
0.63	55.3	473
1.25	68.5	687
2.5	70.7	778
3.75	73.8	843
4.69	73.0	839
4.68	79.5	933
7.82	79.1	991
	[Alcohol] = 0.0131 *M*	
0.62	45.1	434
1.25	53.0	465
2.5	60.0	530
5.0	63.0	583

[a] $[CrO_3] = 1.03 \times 10^{-3}$ *M*, $\mu = 0.183$ *M* ($NaClO_4$), 15.0 ± 0.2°.

In order to interpret the data, it was first necessary to determine the equilibrium constant for the reaction[7]

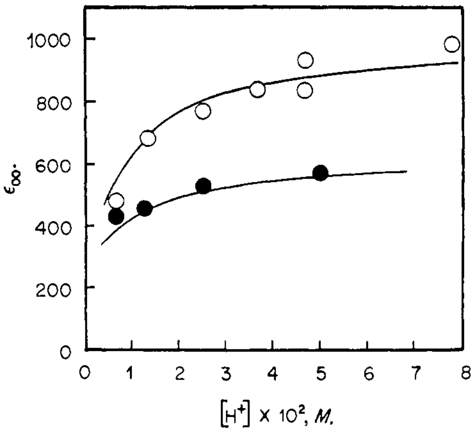
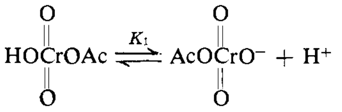


Figure 4. Effect of hydrogen ion concentration on the equilibrium absorbancy indices for the reaction of isopropyl alcohol with chromic acid. The upper points are for 0.030 *M* alcohol, and the lower points are for 0.013 *M* alcohol. The lines represent the calculated values.



$$HO\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}OAc \overset{K_1}{\rightleftharpoons} AcO\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}O^- + H^+$$

This may be estimated spectrometrically using the equation

$$\epsilon_T = \left(\frac{\epsilon_2 - \epsilon_T}{[H^+]}\right)K_1 + \epsilon_1$$

where ϵ_T is the observed absorbancy index, ϵ_2 is the absorbancy index of the acetochromate ion, and ϵ_1 is the absorbancy index of the conjugate acid. At 385 mμ, ϵ_2 was found to be 302 in 97% acetic acid containing enough sodium acetate to convert all of the chromium(VI) to its anion. The experimental data are summarized in Table III. A plot of ϵ_T against $(\epsilon_2 - \epsilon_T)/[H^+]$ gave a straight line from which was obtained $K = 0.026$ and $\epsilon_1 = 418$. We have previously shown[8] that for low acid concentration at a constant ionic strength, H_0 is approximately linearly dependent on log $[H^+]$ in these solutions and that the major effect of changing solvent composition is on the proton level rather than activity coefficients. Therefore, for convenience, we shall use hydrogen ion concentrations rather than H_0 throughout the following discussion.

Table III. Equilibrium Data for Protonation of Acetochromate Ion[a]

$[H^+] \times 10^2$ *M*	ϵ_T	$(\epsilon_2 - \epsilon_T)/[H^+]$
1.25	342	−3200
2.5	360	−2320
5.0	382	−1600
10.0	396	−940

[a] $[CrO_3] = 1.03 \times 10^{-3}$ *M*.

For a higher chromic acid concentration (2.03×10^{-3} *M*), the equilibrium constant was found to be 0.022. The small change in observed equilibrium constant is

---

(7) It is known that chromic acid forms mixed anhydrides with almost any anion present in solution (D. G. Lee and R. Stewart, *J. Am. Chem. Soc.*, **86**, 3051 (1964)), and that significant spectral shifts accompany the structural changes. It is therefore probable that the principal anion is the acetochromate ion. Also, see Experimental Section for the effect of acetic acid on the spectrum of chromium(VI).

(8) K. B. Wiberg and R. J. Evans, *J. Am. Chem. Soc.*, **80**, 3019 (1958).

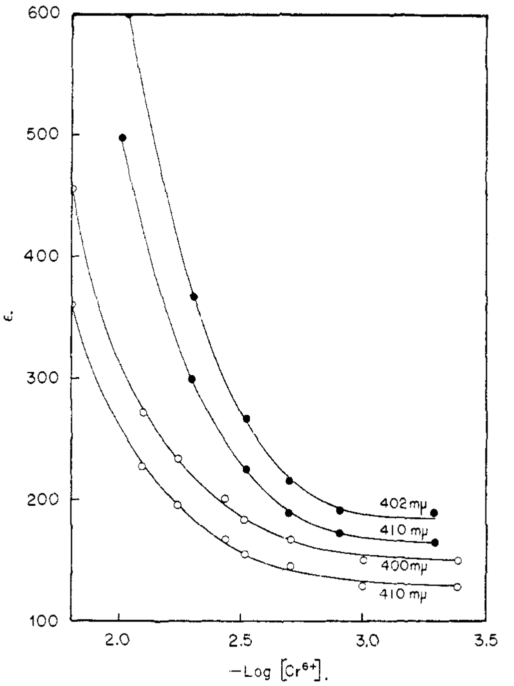


Figure 5. Beer's law plots for chromium(VI) in 91% acetic acid (○) and 97% acetic acid (●).

not unexpected since some of the chromium(VI) will be in the dimer form (see below).

The monomer–dimer equilibrium constant was estimated from the dependence of the absorbancy index

$$2HOCrO_2Ac \rightleftharpoons AcOCrO_2OCrO_2OH + HOAc$$

of chromic acid on its concentration. The equilibrium constant had been determined to be 25 for 91% acetic acid using the deviations from Beer's law.[9] The deviation begins at a lower concentration when 97% acetic acid is used. The beginning of curvature for 97% acetic acid was shifted with respect to that for 91% acetic acid by about 0.25 log unit (Figure 5) which corresponds to a ratio of concentrations of about 1.8. The equilibrium constant is then ~85 in 97% acetic acid, and at the concentration of chromic acid used in the kinetic studies (1.03×10^{-3} *M*), only 7% of the chromium will be in the dimer form. Similarly, an examination of Figure 5 shows that the chromic acid concentration used corresponds to the point where the absorbancy index just begins to increase with increasing concentration. Thus, only a very small amount of dimer should be present. It was concluded that the dimer could be neglected in calculating equilibrium and rate constants.

Since the kinetic data in Table I show that the deuterium-labeled alcohol reacts at the same rate as the unlabeled alcohol, it is clear that the process is not an oxidation.[10] In view of other data,[3,11] it seems reasonable to assume that the reaction is that of ester formation. For example, a similar equilibrium absorbancy index *vs.* alcohol concentration curve is found with *t*-butyl alcohol which is known to form di-*t*-butyl chromate (Figure 6).

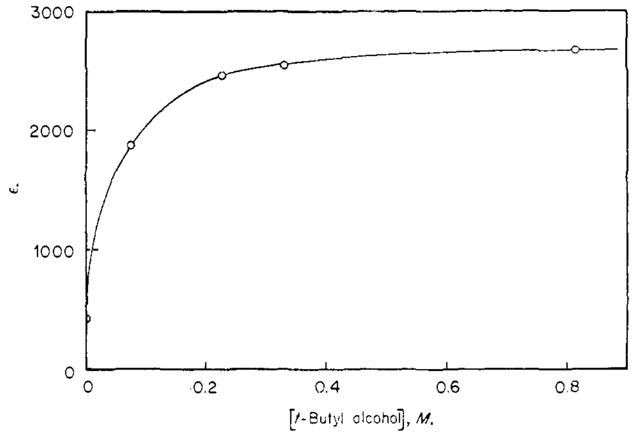


Figure 6. Equilibrum absorbancy indices for the reaction of *t*-butyl alcohol with chromic acid; $[H^+] = 0.0125$ *M*, λ 385 mμ, 97% acetic acid.

The fact that the kinetic curve and the equilibrium absorbancy index curve (Figure 2 and 3) have a discontinuity suggests that monoester and diester formation is being observed. A sequence of reactions and equilibria which seem reasonable is[12]

$$AcOCrO_2OH \rightleftharpoons AcOCrO_2O^- + H^+ \quad K_1 = 0.026$$

$$AcOCrO_2OH + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ROCrO_2OH\ (+\ AcOH)$$

$$ROCrO_2OH \overset{K_3}{\rightleftharpoons} ROCrO_2O^- + H^+$$

$$ROCrO_2OH + ROH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} ROCrO_2OR\ (+\ H_2O)$$

In order to obtain the rate constants for the above sequence, it was first assumed that the rate constants associated with the monoester were such that the equilibrium concentration would be present in each case. The last step is a reversible reaction, and the rate constant will be the sum of the forward and reverse rates. If the fraction of chromium(VI) present as the monoester is designated by f_M, the observed rates would then be given by

$$k_{obsd} = k_4 f_M[ROH] + k_{-4}$$

where

$$f_M = 1.0/(K_1/[ROH][H^+]K_2 + 1.0/[ROH]K_2 + K_3/[H^+] + 1.0)$$

The rate constants could then be obtained from a plot of k_{obsd} against f_M[ROH]. The slope would give k_4 and the intercept would be k_{-4}. The rate constants were obtained for several assumed values of K_2 and K_3, with K_1 set at the value determined experimentally and using the data for $[ROH] > 0.025$ *M*. In the range 250–1000, the value of K_2 had little effect on either k_4 or k_{-4}, and for $K_2 = 500$ and $K_3 = 0$, $k_4 = 555$ and $k_{-4} = 55.6$

---

[9] K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

[10] M. Cohen and F. Westheimer, *ibid.*, 74, 4387 (1952), have found an isotope effect $k_H k_D = 8$ in 86.5% acetic acid.

[11] U. Kläning, *Acta Chem. Scand.*, 11, 1313 (1957); 12, 576 (1958); U. Kläning and M. C. R. Symons, *J. Chem. Soc.*, 3204 (1961), found spectroscopic evidence for ester formation in aqueous solution.

[12] An alternative to step 2 would involve formation of $AcOCr_2OR$ rather than $ROCrO_2OH$. However, one might expect that the less basic anion would preferentially be lost from the acetochromic acid,[7] and the formation of $ROCrO_2OH$ appears to better fit the absorbance data.

giving $K_4 = 10.0$. A change in K_3 had little effect on k_{-4}, and its effect on k_4 is given by

$$k_4 = 555(1.0 + K_3/[H^+])$$

Values for the absorbancy indices may be chosen to fit the equilibrium absorbancy indices for low and high alcohol concentrations.[13] It was then possible to calculate the equilibrium absorbancy index as a function of alcohol concentration using the equilibrium constants given above. The fit was not good, and the curvature was found to be too great suggesting that the equilibrium constant obtained above is too large.

Next, an attempt was made to obtain the equilibrium constants from the equilibrium absorbancy indices. At a constant acid concentration, the ratio of acetochromate ion to acetochromic acid is a constant, and the ratio of the monoester anion to monoester is a constant. Thus, we need only be concerned about the sum of the acetochromate species (A), the sum of the monoester species (M), and the diester (D). The equilibrium constants will be designated as K_2' and K_4' to distinguish them from the true equilibrium constants. Then

$$\epsilon_\infty = f_A\epsilon_A + f_M\epsilon_M + f_D\epsilon_D$$

where

$$f_A = 1.0/(1.0 + K_2'[ROH] + K_2'K_4'[ROH]^2)$$

$$f_M = K_2'[ROH]/(1.0 + K_2'[ROH] + K_2'K_4'[ROH]^2)$$

$$f_D = K_2'K_4'[ROH]^2/(1.0 + K_2'[ROH] + K_2'K_4'[ROH]^2)$$

The value of ϵ_A is known from the acetochromic acid–acetochromate ion equilibrium study. The unknown are then ϵ_M, ϵ_D, K_2', and K_4'. Starting with a set of assumed values, the parameters were adjusted to give a good fit to the experimental data using the method of steepest descent.[14] The fit had only a weak dependence on K_2', and values in the range of 50–150 appeared satisfactory.

A fairly broad minimum was found. However, as would be expected, the fit was strongly affected by K_4', and a value of 6.2 ± 0.2 led to a good fit. The corresponding equilibrium absorbancy indices were ϵ_M 250 and ϵ_D 3400. The rms error was 28 corresponding to about a 3% deviation. The true equilibrium constants may be obtained from

$$K_2 = K_2'(1.0 + K_1/[H^+])/(1.0 + K_3/[H^+])$$

$$K_4 = K_4'(1.0 + K_3/[H^+])$$

The difference between the values of K_4' obtained from the rate constants ($K_4 = 10.0 = K_4'$ for $K_3 = 0$) and from the equilibrium absorbancy indices (6.2) is easily understood. The first value of K_4' was obtained assuming that an equilibrium concentration of monoester will at all times be present. This is, however, not the case. If a lower steady-state concentration of monoester is reached, the observed rate constants will be reduced and the effect will be largest at low alcohol concentrations. This will result in a smaller intercept and a larger slope than would otherwise be expected. In order to compensate for this, the true value of k_{-4} must be greater than that calculated above and correspondingly the true value of k_4 must be smaller than the calculated value. The value of K_4' is then decreased toward that found from the equilibrium absorbancy indices.

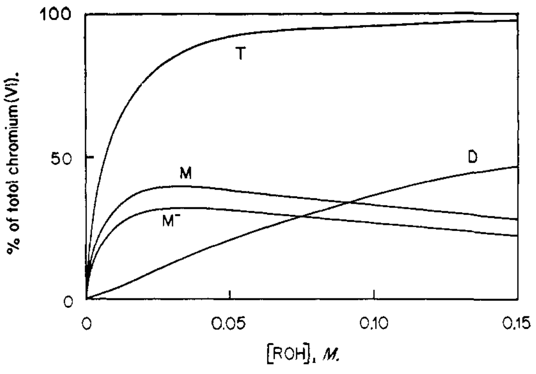


Figure 7. Effect of isopropyl alcohol concentration on the proportions of the chromium(VI) species at 0.0125 *M* acid. M is the monoester, M⁻ is the monoester anion, D is the diester, and T is the sum of these three species.

Having established ranges for the several variables, it was possible to simulate the course of the reaction by numerically integrating the set of differential equations. This was done for each of the sets of concentrations used to obtain the experimental data and the parameters were varied so as to obtain a good fit between observed and calculated rate constants and equilibrium absorbancy indices. The values of k_4 and k_{-4} were easily fixed since the results were quite sensitive to these constants. K_3 did not significantly affect the results at a constant acid concentration. However, the calculated change in the absorbancy index with acid concentration was strongly effected by K_3. A value of 0.01 was independently determined from the effect of acid concentration on rate constants and equilibrium absorbancy indices. K_2 had little effect on the results and was given a value of 250 because this would lead to a satisfactorily large value of k_2. The latter must be at least ten times as large as k_4 for otherwise a marked induction period would be noted in the kinetic studies. The final set of values which gave a good fit to the experimental results was

$$K_1 = 0.026 \pm 0.002$$

$$k_2 \approx 12{,}500 \qquad k_{-2} \approx 50 \qquad K_2 \approx 250$$

$$K_3 = 0.010 \pm 0.002$$

$$k_4 = 780 \pm 20 \qquad k_{-4} = 70 \pm 2 \qquad K_4 = 11.1 \pm 0.4$$

$$(\epsilon \text{ (monoester) } 300)$$

$$(\epsilon \text{ (monoester anion) } 220)$$

$$(\epsilon \text{ (diester) } 3400)$$

The errors associated with the parameters are estimates based on the magnitude of the effect of a variation in the parameter on the agreement between calculated and observed rate constants and absorbancy indices. The value of K_4 corresponds to $K_4' = 6.2$, in good agreement

---

(13) It was assumed that the ratio of the absorbancy indices of the monoester and its anion would be the same as that for acetochromic acid and its anion.

(14) *Cf.* K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, Inc., New York, N. Y., 1965, p 185.

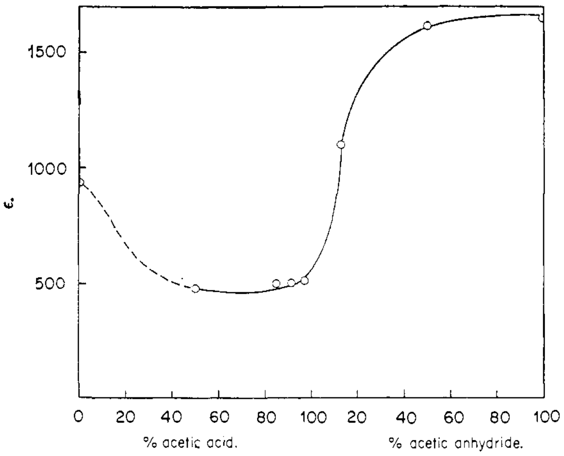


Figure 8. Effect of solvent medium on the absorbancy index for chromium(VI) at 385 mμ.

with that calculated above. The lines in Figures 2, 3, and 4 represent the calculated results.

The concentrations of monoester, monoester anion, and diester were calculated for a number of alcohol concentrations with an acid concentration of 0.0125 *M*. The data are presented in Figure 7. It can be seen that most of the chromium(VI) is in the form of an ester even at relatively low alcohol concentrations. An increase in acid concentration will decrease the amount of monoester anion, and produces a corresponding increase in the mono- and diester concentrations.

Experimental Section

Reagents. Isopropyl alcohol was Fisher reagent grade. No impurities could be detected by vpc. Isopropyl-*α-d* alcohol was prepared by adding 4.35 g of acetone to a mixture of 1 g of lithium aluminum deuteride in 20 ml of dry diglyme at 10°. The mixture was stirred for 2 hr at 50°. A Vigreux column was attached to the flask, 20 ml of ethylene glycol was added, and the mixture was distilled giving 3.3 g (73%) of the alcohol. Vpc analysis indicated 99.6% purity with diglyme as the impurity.

Chromium trioxide, sodium perchlorate, and perchloric acid were analytical reagent. Acetic acid was purified as described previously[9] and contained 0.29% water as determined from freezing point depression.

The solvent was prepared by mixing 9281.4 g of 99.71% acetic acid with 259.3 g of water and 205.56 g of anhydrous sodium perchlorate. This solution, 97% acetic acid by weight with an ionic strength of 0.183 *M* was stored under nitrogen. The perchloric acid solution was prepared by mixing 3381 g of 99.71% acetic acid, 56.2 g of water, 144.5 g of perchloric acid (d = 1.65, 71.6%), and 73.53 g of sodium perchlorate. The calculated concentration of perchloric acid was 0.3124 *M*, and titration gave 0.312 *M*.

Kinetic Method. Solutions were made from the two stock solutions by adding weighed amounts of chromic acid or isopropyl alcohol. The solutions were degassed by freezing, evacuating to 0.1 torr, melting, and filling the flasks with nitrogen. The solutions were placed in the two storage syringes of the stopped-flow apparatus, brought to the correct temperature, and mixed. A 2-mm cell was used throughout. The transmittance of the solution was recorded with a high-speed recorder for the fast runs, and was recorded in digital form on punched paper tape for slower runs. The data were converted to absorbance, and the rate constants were calculated in conventional fashion.

Absorbancy Indices for Diisopropyl and Di-*t*-butyl Chromates. Both chromate esters were prepared in benzene solution by the procedure of Westheimer, Holloway, and Cohen.[15] The absorbance at 385 mμ was determined immediately after preparation, and an aliquot of the solution was analyzed for its chromium(VI) content. In this way, diisopropyl chromate was found to have ε 2740, 2620 (two preparations) and di-*t*-butyl chromate was found to have ε 2960, 2870. The effect of *t*-butyl alcohol on the absorbancy index of chromium(VI) in 97% acetic acid was determined giving the data in Figure 6. From this one finds for the diester ε 2910, and equilibrium constant K = 18.4. The absorbancy index is in good agreement with that measured in benzene.

It should be noted that the absorbancy index for diisopropyl chromate in benzene is a minimum value since the ester decomposes fairly rapidly.

Rates of Acetate Formation. The rate at which isopropyl alcohol reacts with acetic acid in the 97% solvent was determined by vpc analysis of reaction solutions, and by following the change in the α-proton signal in the nmr spectrum. In the absence of added acid, the rate constant (20°) was 1.06×10^{-6} mol l.$^{-1}$ sec^{-1}. With 0.0125 *M* acid, the rate constant was 5.35×10^{-6} and with 0.1 *M* acid, it increased to 2.56×10^{-5}. The rate of reaction was sufficiently slow that no significant fraction of the alcohol would be converted to ester under the reaction conditions.

Change in Chromium(VI) Absorbancy Index with Change in Solvent. The absorbance of chromium(VI) solutions at 385 mμ was determined using a Cary 14 spectrometer using a series of acetic acid–water and acetic acid–acetic anhydride mixtures. The water-containing solutions had sufficient perchloric acid to maintain H_0 at −0.313, and the ionic strength was maintained at 0.32 *M* with sodium perchlorate. The data are summarized in Figure 8. It is seen that the species formed in aqueous acetic acid has a lower absorbancy index than chromic acid or diacetyl chromate. This suggests that the species present in the acetic acid–water mixtures is acetochromic acid and indicates that no significant amount of diacetyl chromate is present so long as the solvent contains water.

Monomer–Dimer Equilibrium Constant. If A is the dimeric chromium(VI) species, B is the monomeric species, and C is the total chromium(VI) concentration, the equilibrium constant is given by

$$K = \frac{A}{B^2} = \frac{A}{(C - 2A)^2}$$

Neglecting A^2 one finds $A = KC^2/(1 + 2KC)$. At points of equal slope, A_1 (91% acetic acid) $\cong A_2$ (97% acetic acid). Then

$$\frac{K_1C_1^2}{1 + 2K_1C_1} = \frac{K_2C_2^2}{1 + 2K_2C_2}$$

With $K_1 = 25$, $C_1 = 3.2 \times 10^{-3}\,M$, $C_2 = 1.8 \times 10^{-3}\,M$, one finds $K_2 \cong 85$. For [Cr^{6+}] = $1.0 \times 10^{-3}\,M$, the fraction of dimer is then 7%. Judging from the shape of the curves on Figure 5, this would appear to be an upper limit.

---

[15] F. H. Westheimer, F. Holloway, and M. Cohen, *J. Am. Chem. Soc.*, 73, 65 (1951).