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The Chromic Acid Oxidation of Isopropyl Alcohol in 86.5% Acetic Acid Solution. The Chemistry of the Chlorochromate Ion

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The chromic acid oxidation of isopropyl alcohol in 86.5% acetic acid is first order in the alcohol, in acid chromate ion and in hydrogen ion, but proceeds 2500 times as fast as in water. The relative rates of oxidation of $CH_3CDOHCH_3$ and of $CD_3CHOHCD_3$, compared to that of $CH_3CHOHCH_3$ are the same as in water. The mechanism for the oxidation is therefore probably the same as in aqueous solution. The oxidation is strongly inhibited by chloride ion, and in the presence of chloride ion the ultraviolet absorption spectrum of chromic acid in acetic acid is modified. Both the spectroscopic data and the kinetic data for the reaction in the presence of chloride ion can be correlated with an equilibrium constant of 1×10^{-5} (mole/liter)$^{-2}$ for the reaction $H^+ + Cl^- + HCrO_4^- \rightleftarrows ClCrO_3^- + H_2O$ together with the assumption that the chlorochromate ion is a poor oxidizing agent (as compared with the acid chromate ion) for isopropyl alcohol.

Introduction

In dilute aqueous solution and in aqueous acetic acid solution, chromic acid oxidizes isopropyl alcohol to acetone. The mechanism for the oxidation in aqueous solution has been fairly well elucidated; the reaction proceeds by way of the chromic acid ester of the alcohol.[1,2] The present work was undertaken in an attempt to elucidate the mechanism of the reaction in aqueous acetic acid as solvent. Many of the preparative oxidation reactions with chromic acid have been carried out in this latter solvent, but the kinetic results previously available[3] do not answer the questions of mechanism here considered.

The oxidation of isopropyl alcohol in acetic acid is extremely rapid and, at moderate alcohol and acid concentrations, could not be followed accurately by ordinary techniques. The addition of water to glacial acetic acid sharply decreases the rate of acid-catalyzed oxidation, and further permits the solution to be cooled, without freezing, to temperatures below 16°. The solvent chosen (86.5% acetic acid, 13.5% water by weight) remains liquid at 0°. In this solvent and at this temperature, the rate can easily be followed spectrophotometrically. The acidities of various solutions in this solvent were determined by an indicator method, and described in terms of Hammett's H_0 function.[4] Although this function is in general useful only for studies where a proton is added to an uncharged base, and although in the present work the "base" may be regarded as the anion, $HCrO_4^-$, the H_0 function is nevertheless a proper measure of acidity. All the solutions were measured in the same solvent and at the same ionic strength; there is then no change, in going from one solution to another, in the relative base strengths of charged and of uncharged bases.

Experimental

Materials.—Commercial isopropyl alcohol was dried over lime and fractionated through a 24″ distilling column packed with single turn glass helices; the product had a boiling point constant to ±0.05°. Niacet C.P. acetic acid was distilled from 1% by weight of chromic acid, and fractionated through the same column; it boiled at 118.0 ± 0.2° at 750 mm. Chromic acid was twice recrystallized from water and dried over P_2O_5 in vacuum. Sodium perchlorate was twice recrystallized from water, and gave a negligible test for chloride ion. Sodium benzenesulfonate was prepared from the purified barium salt by passing the latter, in aqueous solution, over Amberlite IR-120 in the sodium form. The salt, twice recrystallized from water, gave a negligible test for chloride ion. White label Eastman Kodak Company *p*-nitroaniline was twice recrystallized from alcohol. Benzeneazodiphenylamine[5] melted at 87–88°; hypochlorous acid was prepared according to Ballard.[6] Other chemicals were of reagent grade. 2-Deuteropropanol-2 and 1,1,1,3,3,3-hexadeuteropropanol-2 were supplied by A. Leo.[7]

Rate Measurements.—The disappearance of Cr^6 was followed spectrophotometrically at 3500 Å. in a thermostated compartment[8] attached to a Beckman model DU quartz spectrophotometer. Bakelite blocks, supplied by the National Technical Laboratories were used to insulate the thermostat compartment from the monochromator and phototube housings of the spectrophotometer. A stream of cold, dry air was passed through the cell compartment, and served to prevent condensation of moisture on the faces of the cells. The temperature in the absorption cells was held to 0.3 ± 0.1° with circulating ice-water.

All chromic acid and isopropyl alcohol solutions in 86.5% acetic acid were made up directly before use; the rates of oxidation of the solvent by chromic and perchloric acids and of esterification of isopropyl alcohol by the solvent were negligible compared to the rate measured. The reacting solutions were cooled before mixing, and then transferred to a 10-mm. corex absorption cell, which in turn was placed in the thermostat compartment. When the chromic acid solutions were moderately concentrated, 9 mm. quartz blocks were inserted in the corex cells, reducing the light path to 1 mm. During the operation of filling the cell, the solutions warmed somewhat, and the initial rates were therefore always greater than those which later obtained. In general, the observations taken during the first ten minutes were disregarded for this reason; this practice was of course trivial for the reactions with long half-lives, but important for those with short half-lives. The average deviation of twelve similar rate constants, determined over a period of a year, was ± 3%. This mean value agreed with that obtained from a rate experiment where the reaction was followed iodimetrically. Reactions with half-lives of several days were kept at 0° in a Dewar, rather than at +0.3° in the thermostated Beckman cell.

Oxygen Effect.—Waters[9] has reported that some chromic acid oxidations in acetic acid solution are profoundly affected by the presence of oxygen. A few experiments were therefore conducted in an evacuated apparatus, sealed to a short piece of ten mm. optically polished square Pyrex tubing. The solutions were mixed after they had been thoroughly degassed, and the rate of oxidation was measured spectrophotometrically. The rates were the same, within about 10%, as those measured in air.

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[1] F. Holloway, M. Cohen and F. Westheimer, THIS JOURNAL, **73**, 65 (1951).

[2] F. Westheimer, *Chem. Revs.*, **45**, 419 (1949), and Errata, June, 1950.

[3] R. Slack and W. Waters, *J. Chem. Soc.*, 1666 (1948); 599 (1949).

[4] L. Hammett and A. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[5] H. Torrey and W. MacPherson, *ibid.*, **31**, 579 (1909).

[6] A. Ballard, *Ann. chim. phys.*, **57**, 225 (1834).

[7] A. Leo, Ph.D. Dissertation, Chicago, 1952; A. Leo and F. Westheimer, THIS JOURNAL, **74**, 4383 (1952).

[8] P. Bell and C. Stryker, *Science*, **105**, 415 (1947).

[9] W. A. Waters, *Trans. Faraday Soc.*, **42**, 184 (1946).

Measurements of Acidity.—The acidity was measured according to the general method of Hammett and Deyrup.[4] The indicators (*p*-nitroaniline and benzeneazodiphenylamine) were used at concentrations of 6 × 10^{-4} mole/liter; this relatively high indicator concentration necessitated the use of quartz inserts to shorten the light path in the absorption cells. Benzeneazodiphenylamine has two colored forms, with absorption maxima at 5380 and 4100 Å., respectively, for the acid and base forms. The indicator is largely converted to the acid form by perchloric acid in 86.5% acetic acid, and largely converted to the base form by a solution of sodium acetate in this solvent. The data are consistent with the values for the extinction coefficients of the acid and base forms as follows.

$$E_a(5380\ \text{Å.}) = 60,500 \qquad E_b(5380\ \text{Å.}) = 700$$
$$E_a(4100\ \text{Å.}) = 780 \qquad E_b(4100\ \text{Å.}) = 27,400$$

Products.—Ten ml. of a solution 1.5 molar in isopropyl alcohol, 0.1 molar in CrO_3 and 0.1 molar in perchloric acid was allowed to react until the yellow color of the chromic acid disappeared. A 2-ml. aliquot of this solution was pipetted into 50 ml. of a 2 *N* HCl solution saturated at 0° with 2,4-dinitrophenylhydrazine; ten cc. of 2 *N* HCl was added to ensure the solubility of the hydrazine. After 30 minutes at 0°, acetone 2,4-dinitrophenylhydrazone was collected, washed, dried and weighed. Yields of acetone 2,4-dinitrophenylhydrazone were 94 ± 2% of theoretical; control experiments with pure acetone gave yields of 96 ± 1%. The derivative melted at 121–122°; after one recrystallization, it melted at 124–125°. The acetone 2,4-dinitrophenylhydrazone prepared in the control experiments behaved in the same manner.

Results

Kinetics of the Oxidation in the Absence of Chloride Ion.—The values of the H_0 function, and the approximate hydrogen ion concentrations for various solutions are shown in Table I.

TABLE I

H_0 FUNCTION IN 86.5% ACETIC ACID

Perchloric acid, m./l.	Indicator	H_0	(H^+) m./l.
0.0920	*p*-Nitro-	0.22	0.0921
.0460	aniline	.56	.0462
.0230		.86	.0234
.0115		1.15	.0122
.000		1.71	.00303
Sodium acetate, m./l.			
0.000	Benzene-	1.71	0.00303
.0115	azodiphenyl-	2.33	.000755
.0230	amine	2.62	.000323
.0460		2.96	.000199
.0920		3.41	.000100

From these data, the auto protolysis constant of 86.5% acetic acid was estimated as 0.9 × 10^{-5} (mole/liter)^2.

Although toe acidities shown in Table I were approximately constant during any particular experiment, it is nevertheless true that the oxidation reaction consumes hydrogen ions, and that the concentration of these ions therefore changes during the reaction.

$$2HCrO_4^- + 3CH_3CHOHCH_3 + 8H^+ \longrightarrow 2Cr^{+++} + 3CH_3COCH_3 + 8H_2O \quad (1)$$

$$Cr^{+++} + 3HOAc \rightleftarrows Cr(OAc)_3 + 3H^+ \quad (2)$$

When very dilute chromic acid solutions were used in the presence of relatively large quantities of perchloric acid or of sodium acetate, the hydrogen ion concentration remained essentially constant during any one experiment. However, reactions conducted with dilute chromic acid solutions in the absence of added strong acid or base, or still worse, reactions conducted with unbuffered concentrated solutions of chromic acid, are necessarily accompanied by large changes in acidity. Failure to take these changes in acidity explicitly into account can lead to considerable kinetic difficulties.[5] On the other hand, it is not a simple matter to take the changes in acidity explicitly into account because the position of the equilibrium (equation 2) varies with acidity; preliminary measurements show that in strong perchloric acid solutions, three hydrogen ions are consumed for each molecule of chromic acid which reacts, whereas in weak acid solutions, only one hydrogen ion per chromic acid molecule is consumed.[10] The present experiments were therefore restricted to those solutions where the chromic acid concentration was very low, and where, therefore, only a small change in acidity occurred during the oxidation process. In each individual rate experiment, the concentration of isopropyl alcohol was high compared to that of the chromic acid. Since (for the reasons given above) the hydrogen ion concentration could also be regarded as constant, the individual rate experiments could be regarded as first order reactions.

$$v = k_3(H^+)(CH_3CHOHCH_3)(CrO_3) = k_2(CH_3CHOHCH_3)(CrO_3) = k(CrO_3) \quad (3)$$

The values of *k*, obtained by graphical methods from the actual rate data, and the values of k_2 calculated from them, are presented in Table II.

TABLE II

RATES OF OXIDATION OF ISOPROPYL ALCOHOL BY CHROMIC ACID AT AN IONIC STRENGTH OF 0.125 AND AT 0°

CrO_3	$HClO_4$	NaOAc	*i*-PrOH	10^4k, sec.$^{-1}$	10^4k_2, sec.$^{-1}$ (m./l.)$^{-1}$
0.00100	0.023	...	0.0655	3.59	54.9
.00100	.023	...	.131	6.78	51.8
.00100	.023	...	.262	12.4	47.3
.00100	.023	...	.524	24.0	45.9
0.00750	0.023	...	0.131	5.61	42.9
.00200	.023	...	.131	6.49	49.5
.00100	.023	...	.131	6.78	51.8
.00050	.023	...	.131	6.86	52.3
.00030	.023	...	.131	7.19	54.9
0.00100	0.046	...	0.131	13.9	106
.00100	.023	...	.131	6.78	51.8
.00100	.0115	...	.131	3.49	26.6
.00100	....	...	.131	0.902	6.89
.00100	....	0.114	.131	.250	1.91
.00100	....	.225	.131	.130	0.99
.00100	....	.452	.131	.071	0.54

It is clear from the constancy of the values of k_2 over about tenfold variations in the concentrations of alcohol and of chromic acid, that the reaction is essentially first order in alcohol and in chromic acid. In the concentration range investigated, there is no real kinetic evidence for the formation of $Cr_2O_7^=$. The slight decrease in rate at higher chromic acid concentrations is probably due to a lower average hydrogen ion concentration during the reaction.

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(10) M. Cohen, Ph.D. Dissertation, University of Chicago, 1951.

The dependence of rate on hydrogen ion concentration is shown in Fig. 1, where the values of log k_2 are plotted against H_0; the solid line, drawn with a slope of -1, corresponds to the theoretical line for a reaction first order in hydrogen ion.

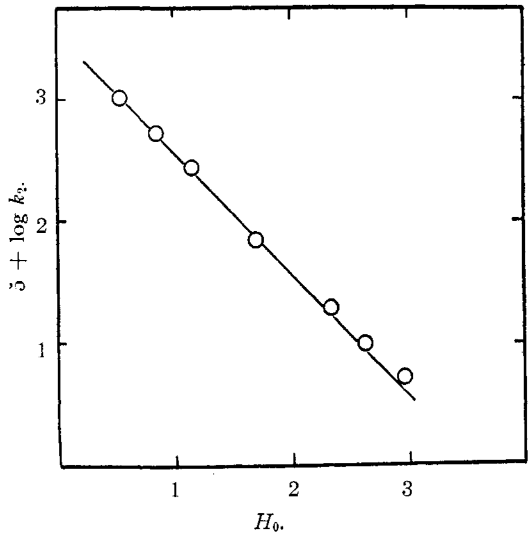

Fig. 1.—Relationship between acidity and second order rate constants, k_2 (see Table II).

Diminution of Rate in the Presence of Chloride Ion.—A diminution of rate of chromic acid oxidations in the presence of chloride ion has previously been noted.[11] In the present investigation, the effect was large (Fig. 2); when the perchloric acid and chloride ion concentrations were high, the rate of oxidation was less than two per cent. of that which was obtained in the absence of chloride. The effect of chloride ion on the reaction is not due to its basicity; it had no effect upon the measured H_0 values of 86.5% acetic acid solutions. Nor is the effect due to chain reactions in which chloride ion is oxidized to hypochlorite, since hypochlorous acid has no effect upon the reaction. But the effect of chloride ion upon the reaction rate can be explained in terms of the equilibrium

$$H^+ + Cl^- + HCrO_4^- \rightleftarrows ClCrO_3^- + H_2O \quad (4)$$

plus the additional assumption that chlorochromate ion is a poor oxidizing agent relative to acid chromate ion. Potassium chlorochromate[12] is a known substance; chromyl chloride can be made by adding chromic acid to concentrated aqueous hydrochloric acid.

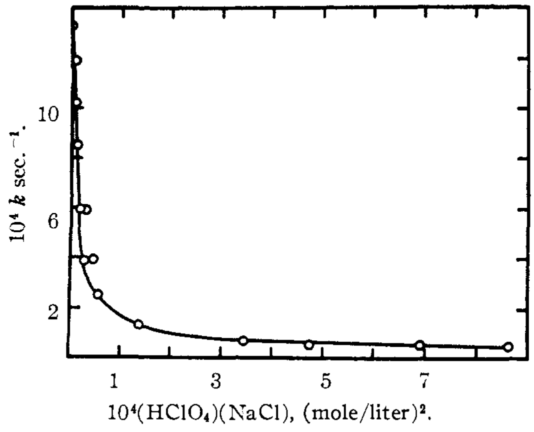

Fig. 2.—Relationship between the $(H^+)(Cl^-)$ product and the observed first order rate constant; $(CrO_3) = 0.0005$ mole/liter, $(CH_3CHOHCH_3) = 0.26$ mole/liter.

The evidence that the chlorochromate ion is involved in the oxidation process here described consists of two parts (a) a new species can be detected spectrophotometrically in aqueous acetic acid solutions of perchloric acid, chloride ion and chromic acid, and (b) mathematical analysis of the kinetics leads to a value of the equilibrium constant for equation (4) essentially identical with that found spectrophotometrically.

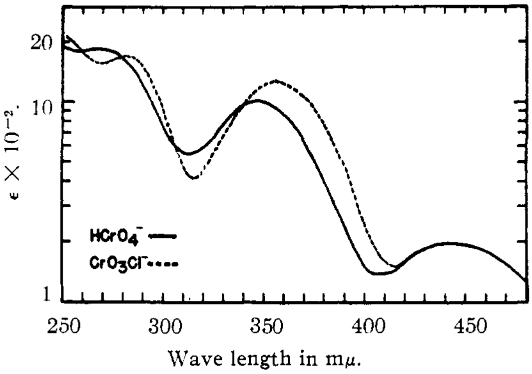

Fig. 3.—Spectra of $HCrO_4^-$ and of $ClCrO_3^-$.

(a) **Spectroscopic Evidence.**—The addition of chloride ion to solutions of chromic acid in 86.5% acetic acid causes a change in the characteristic spectrum of chromic acid (Fig. 3). At constant perchloric acid concentration, the magnitude of the spectral change increases, up to a definite limit, with increasing chloride ion concentrations. Furthermore, at constant chloride ion concentration the magnitude of the spectral change increases, up to the same definite limit, with increasing perchloric acid concentrations; in the presence of sodium acetate, the spectra in the presence and in the absence of chloride ion are identical. These facts are qualitatively in accord with those predicted from equation (4). If it is assumed that the limiting spectrum obtained at high acid and high chloride ion concentrations is that of the chlorochromate ion, it is then possible to calculate from the spectra obtained at intermediate concentrations of acid and chloride ion, the equilibrium constant

$$(ClCrO_3^-)/(H^+)(HCrO_4^-)(Cl^-) = K \quad (5)$$

Three solutions (where the ratio of $ClCrO_3^-$ to $HCrO_4^-$ varied from three to one-third) gave values of the equilibrium constant of $1.11 \pm 0.11 \times 10^5$ (moles/liter)$^{-2}$. The variation in K is largely a variation with the wave length at which the measurements were made; the results at three wave lengths (3550, 3800 and 3900 Å.) were averaged. The constancy of the equilibrium constant shows

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[11] M. Bobtelsky and C. Radovensky-Cholatnikow, *Z. anorg. u. allgem. Chem.*, **199**, 241 (1931); F. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

[12] L. Helmholz and W. Foster, THIS JOURNAL, **72**, 4971 (1950).

that little chromyl chloride was present in these solutions; perhaps at still higher acidity and chloride ion concentrations, this latter compound would be stable.

The absorption spectrum of the chlorochromate ion is closely analogous to that of the chromic acid–phosphoric acid complexes studied by Holloway.[13]

(b) **Kinetic Evidence.**—The kinetic effect of chloride ion upon the rate of oxidation of isopropyl alcohol has been observed only in those solutions where the presence of chlorochromate ion has been detected spectrophotometrically. Specifically, in solutions which contain sodium acetate (and where therefore the hydrogen ion and chlorochromate ion concentrations are low) chloride ion has no effect upon the reaction rate. Furthermore, at constant chloride ion concentration, the effect of chloride ion is larger the higher the concentration of perchloric acid. The mathematic analysis of the reaction kinetics is described below in detail. Table III gives the observed and calculated values of the rate constants in the various perchloric acid–sodium chloride solutions. The calculated values were obtained by assigning to the equilibrium constant, K, the value of 1.0×10^5 (moles/liter)$^{-2}$ and a rate constant for the oxidation of isopropyl alcohol by chlorochromate ion of 0.267×10^{-4} sec.$^{-1}$. The value of the equilibrium constant, determined kinetically, is thus in good agreement with that obtained spectrophotometrically.

TABLE III

RATES OF OXIDATION OF ISOPROPYL ALCOHOL IN 86.5% ACETIC ACID AT 0° IN THE PRESENCE OF CHLORIDE ION

$\mu = 0.125$ (unless otherwise noted); $Cr^6 = 0.000500$ m./l. (unless otherwise noted); isopropyl alcohol = 0.262 m./l.; $T = 0.3°$

Expt. No.	Concentrations, mole/liter HClO$_4$	Average (H$^+$)	NaCl	$10^4k_{obsd.}$ (sec.$^{-1}$)	$10^4k_{calcd.}$ (sec.$^{-1}$)
1	0.152	0.152	0.0985	0.206	0.267[a]
2	.0920	.0920	.0150	.342	.365
3	.0460	.0460	.0105	.530	.550
4	.115	.115	.00750	.450	.427
5	.0920	.0920	.00750	.478	.467
6	.0460	.0460	.00750	.651	.667
7	.0920	.0920	.00525	.585	.558
8	.0460	.0460	.00300	1.38	1.34
9	.0230	.0226	.00250	2.48	2.24
10	.0115	.0116	.00250	3.84	3.74
11	.00575	.00643	.00250	5.88	5.50
12	.0920	.0892	.000540	3.80	3.70[b]
13	.0460	.0440	.000540	5.90	5.40[b]
14	.0230	.0200	.000540	8.44	9.68[b]
15	.0115	.0110	.000540	10.2	10.4[b]
16	.0230	.0216	.000216	11.8	12.0[b]
17	.0230	.0229	.000000	13.3	13.3

[a] Initial ionic strength was 0.251. Rate constants were corrected to an ionic strength of 0.125. [b] Initial Cr^6 concentration was 0.00100 m./l.

Isotope Effect.—The rate of oxidation of 2-deuteropropanol-2 in aqueous solution is only about $^1/_7$ that of isopropyl alcohol.[14,7] A. Leo[7] also prepared 1,1,1,3,3,3-hexadeuteropropanol-2 and observed that it is oxidized at almost the same rate as is ordinary isopropyl alcohol. The rate data obtained with these isotopic alcohols in 86.5% acetic acid parallel those found in aqueous solution.

TABLE IV

ISOTOPE EFFECT ON THE RATE OF OXIDATION IN 86.5% ACETIC ACID AT 0°

Alcohol	Concn. m./l.	Ox. agent	H$^-$, m./l.	10^4k_D, sec.$^{-1}$	10^4k_H, sec.$^{-1}$	k_H/k_D
2-Deutero-propanol-2	0.114	$HCrO_4^-$	0.0450	1.50	11.6	7.7[a]
	.073	$HCrO_4^-$	.0457	0.883	7.50	8.7[a]
	.102	$ClCrO_3^-$	.152	0.0441	0.425	9.6[b]
1,1,1,3,3,3-Hexadeuteropropanol-2	.0405	$HCrO_4^-$	.0230	1.99	2.12	1.10[a]

[a] $T = 0.3°$, $\mu = 0.125$. [b] $T = 0.0°$, $\mu = 0.250$.

Discussion

The data obtained in the absence of chloride ion show that the reaction kinetics in 86.5% acetic acid are very similar to those obtained in water as solvent. The isotope effect demonstrates that the rate controlling step in both solvents involves the cleavage of the secondary carbon–hydrogen bond. The reaction in 86.5% acetic acid proceeds smoothly to completion. No difficulties were observed comparable to those previously reported by Waters[3] for the oxidation of diphenylmethane in acetic acid solution. The sharp diminution in rate observed when isopropyl alcohol is oxidized by chromic acid alone in 86.5% acetic acid can be ascribed wholly to the decrease in acidity which accompanies the reaction, and which results from the fact that, in the absence of added mineral acid, chromic acid must supply hydrogen ions as well as the oxidizing species. However, it is quite possible that the situation in glacial acetic acid[3] is much more complex.

The data obtained in the presence of chloride ion show that the retardation of rate in the presence of Cl^- is due to the formation of the chlorochromate ion, which oxidizes isopropyl alcohol, but at a rate much slower than that observed for acid chromate ion itself.

The two principal problems raised by this research are these: (a) why is the rate of oxidation in acetic acid as solvent more than 250 times as fast as in an aqueous solution of the same acidity, as measured by the H_0 function (2500 times as fast as the same hydrogen ion concentration); and (b) why is the chlorochromate ion less effective than the acid chromate ion as an oxidizing agent. Tentative answers to both the questions can be given in terms of the ester mechanism for chromic acid oxidation.[1] Since the equilibrium position for esterification is independent of path, it is permissible to regard the esterification as occurring in the steps

$$HCrO_4^- + H_3O^+ \rightleftarrows H_2CrO_4 + H_2O \qquad (6)$$

$$H_2CrO_4 + CH_3CHOHCH_3 \rightleftarrows (CH_3)_2CHOCrO_3H + H_2O \qquad (7)$$

In the rate controlling step of the oxidation reaction, the ester, A, decomposes according to equation (8)

$$\underset{(A)}{(CH_3)_2CHOCrO_3H} + H_2O \longrightarrow (CH_3)_2CO + HCrO_4^- + H_3O^+ \qquad (8)$$

(The subsequent reactions of the compound of tetravalent chromium have been discussed else-

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[13] F. Holloway, THIS JOURNAL, **74**, 224 (1952).

[14] F. Westheimer and N. Nicolaides, *ibid.*, **71**, 25 (1949).

where.[15]) The position of the equilibrium in equation (6) will be shifted toward the right in a solvent (such as 86.5% acetic acid) with a low dielectric constant. The equilibrium in equation (7) will also be shifted to the right (by a simple mass-action effect) when the solvent is changed from water to aqueous acetic acid. The concentration of the ester, A, should therefore be much greater in the solvent of low dielectric constant than in water. However, the rate of decomposition (equation 8) of the ester, A, into ions will be somewhat less in the solvent of low than in the solvent of high dielectric constant. Nevertheless, on balance, the effect of the solvent on the equilibrium processes, (6) and (7), will be greater than its effect on the rate process, (8), because the ions of equation (6) are more highly polar than is the activated state involved in the reaction shown in equation (8). Therefore an increase in rate can be anticipated as the dielectric constant of the solvent is reduced.[16]

A similar argument may explain the relatively low activity of the chlorochromate ion. Here the esterification and decomposition are represented by the equations

$$ClCrO_3^- + H_3O^+ \rightleftharpoons ClCrO_3H + H_2O \qquad (9)$$

$$ClCrO_3H + CH_3CHOHCH_3 \rightleftharpoons (CH_3)_2CHOCrO_2Cl + H_2O \qquad (10)$$

$$\underset{(B)}{(CH_3)_2CHOCrO_2Cl} + H_2O \longrightarrow (CH_3)_2CO + CrO_2Cl^- + H_3O^+ \qquad (11)$$

The esterification equilibria, (7) and (10), may have about the same equilibrium constant (*cf.* those for acetic and chloroacetic acids), but the strength of the chloroacid will probably be greater[17] and therefore the concentration of the chloroacid will probably be less than that for chromic acid itself. Of course, the same electrostatic effect which makes the chloroacid stronger than chromic acid will make reaction (11) faster than reaction (8). But since the Cr–Cl dipole is closer[18] to the ionizable proton of the acid than to the proton lost from the ester, B, the electrostatic effect on the ionization will be greater than that on the decomposition; the net result must be that the chlorochromate ion is a less efficient oxidizing agent than is the acid chromate ion.

It is of course possible that, in aqueous acetic acid, most of the chromic acid is present as $CH_3CO_2CrO_3H$; in the absence of definite evidence, however, the possible effect of this compound has been neglected. In 86.5% acetic acid, little or no undissociated H_2CrO_4 is present.[19]

Appendix

For the analysis of the kinetic data in the presence of chloride ion, it was assumed that

$$-d(Cr^6)/dt = k(HCrO_4^-) + k_{Cl}(CrO_3Cl^-) = k_{obsd.}(Cr^6) \qquad (12)$$

and that

$$K = (CrO_3Cl^-)/(H^+)(Cl^-)(HCrO_4^-) \qquad (13)$$

Let $x = (HCrO_4^-)$, $a = (HCrO_4^-) + (CrO_3Cl^-)$, $c = (NaCl)_{initial}$. Then

$$x = [-K(H^+)c + K(H^+)a - 1]/2\,K(H^+) + \sqrt{[K(H^+)c - K(H^+)a + 1]^2 + 4K(H^+)a}/2K(H^+) \qquad (14)$$

From equation (12) it follows that $k_{obsd.} = (k - k_{Cl})x + k_{Cl}a$.

Although equations (12) and (14) describe the data correctly for all values of the chloride and hydrogen ion concentrations (provided only that they do not change appreciably during any particular experiment), for certain special situations some approximations are convenient. When both the acidity and the chloride ion concentrations are high, the radical in equation (14) can be expanded in rapidly converging series, and

$$x = a/[K(H^+)c - K(H^+) + 1)] \qquad (15)$$

so that

$$k_{obsd.} = \frac{k}{K(H^+)c - K(H^+)a} + k_{Cl} \qquad (16)$$

From experiments 2–8 and 13 in Table III, and equation (16), the values of $K = 1.0 \times 10^5$ (mole/liter)^2 and $k_{Cl} = 0.267 \times 10^{-4}$ sec.$^{-1}$ were obtained by the method of least squares.

Where the chloride ion concentration is high but the acidity low, the contribution by the chlorochromate ion to the rate is negligible, and the approximation of equation (15) is valid. Therefore

$$k_{obsd.} = k/[K(H^+)c - K(H^+)a + 1] \qquad (17)$$

From experiments 9, 10 and 11, and equation (17), the value of K was calculated as 0.9×10^5 (mole/liter)^2, in good agreement with the other kinetic and the spectrophotometric values of this constant.

Finally, in the region of low chloride ion concentrations and low acidity, equation (14) was solved explicitly for x. Then

$$k_{obsd.} = (x/a)k \qquad (18)$$

The average value of x/a for any experiment was chosen. The data so calculated are shown in Table III. **Figure** 3 presents the data only approximately, since the rate is not controlled exclusively by the $(Cl^-)(H^+)$ product, but rather by the more complicated expressions here developed.

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[15] W. Watanabe and F. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).

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