Intrinsic Viscosities.—The intrinsic viscosities of all samples are plotted against number-average molecular weight in Fig. 4, together with values for several other linear fractions from unpublished data. For the cross-linked samples, $[\eta]$ increases much faster than for the linear samples. This is primarily due to a distortion of the molecular weight distribution function and the fact that $[\eta]$ reflects an average which is closer to $\bar{M}_w$ than to $\bar{M}_n$. The weight average molecular weights of the cross-linked samples can be estimated by an equation due to Stockmayer,[13] which is in our notation $\bar{M}_w = \bar{M}_w^0/(1 - \rho_E\bar{M}_w^0/M_0)$, taking M_w^0 as approximately equal to $\bar{M}_n^0$. When the intrinsic viscosities are plotted against the estimated weight average molecular weights, the linear and cross-linked samples fall much closer together.

Values of μ.—The thermodynamic constant μ is expected to increase with cross-linking.[14,15] However, in our results this effect is barely perceptible (Table I).

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Summary

1. A copolymer of styrene and maleic anhydride has been cross-linked in concentrated dioxane solutions by hexamethylene glycol and by benzidine. The proportion of anhydride groups reacted, ρ_T, was calculated from the amount of cross-linking agent added, and the proportion reacted to form intermolecular linkages, ρ_E, was calculated from the change in number-average molecular weight.

2. The ratio ρ_E/ρ_T decreased with decreasing concentration of polymer during reaction. The data for benzidine were in rough agreement with an approximate theory based on estimating the volume pervaded by a single polymer coil from intrinsic viscosity. The data for hexamethylene glycol showed a deviation which is attributed to a tendency to chelate linkage on the polymer.

MADISON, WISCONSIN RECEIVED JUNE 21, 1950

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[A CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Mechanism of the Chromic Acid Oxidation of Isopropyl Alcohol. The Chromic Acid Ester[1]

BY FRANK HOLLOWAY, MERRILL COHEN AND F. H. WESTHEIMER

Introduction

A series of investigations[2,3,4,5] carried out over the past eleven years has suggested that the chromic acid oxidation of isopropyl alcohol takes place by way of an ester of chromic acid. In dilute acid, the proposed mechanism[1,5] is as follows

$$HCrO_4^- + CH_3CHOHCH_3 + H^+ \underset{}{\overset{\text{rapid}}{\rightleftarrows}} (CH_3)_2CHOCrO_3H + H_2O \quad (1)$$

$$B + (CH_3)_2CHOCrO_3H \xrightarrow[\text{determining}]{\text{rate}} BH^+ + (CH_3)_2CO + HCrO_3^- \quad (2)$$

Here the symbol B represents a molecule of water or of some other base. The scheme here outlined corresponds to the correct kinetics in dilute aqueous acid: the rate is first order in the acid chromate ion,[2] in alcohol[2] and in hydrogen ion. (In more concentrated acid solutions, the reaction rate is second order in hydrogen ion,[2] and the ester must be further protonated.) The mechanism of equations (1) and (2) also corresponds to the fact that the first unstable chromium intermediate is a compound of tetravalent chromium[3]; the subsequent reactions of the tetravalent chromium compound are discussed elsewhere.[3,5] Furthermore, the mechanism here advanced explains the fact[4] (determined from studies with $CH_3CDOHCH_3$) that the rate controlling step of the oxidation involves the cleavage of the C–H bond.

The data, here reported, consist of two parts. (I) A chromic acid ester of isopropyl alcohol can be prepared in benzene or toluene solution; in these solvents the ester is decomposed rapidly by bases (such as pyridine) to form acetone. (II) In aqueous solution (where the base, B, of equation (2) is generally water) the reaction is also catalyzed by pyridine. The relationship of these new facts to the mechanism represented by equations (1) and (2) is then discussed.

I. Chromic Acid Esters

Di-*t*-butyl chromate[6] and several analogous chromic acid esters[6,7] of tertiary alcohols have been prepared by Wienhaus and others. Wienhaus pointed out that when an aqueous solution of chromic acid and of a secondary alcohol was shaken with hexane or carbon tetrachloride, an unstable yellow compound was extracted into the non-aqueous layer. Presumably this was an ester of chromic acid and the secondary alcohol; the extreme ease with which the esters decompose in

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these solvents prevented any extensive work with them. It has now been discovered, however, that the esters can be extracted from aqueous solutions of chromic acid and secondary alcohols by benzene or toluene and in these solvents the esters are somewhat more stable. Although all attempts to isolate the solid esters have so far failed, and although the esters are decomposed photochemically and spontaneously, dilute solutions of the esters in dry benzene or dry toluene can be handled at room temperature and in dim light for about half an hour.

The ester, in solutions of the order of 0.0002–0.002 molar, is bright yellow; the color approximates in quality that of aqueous chromic acid. The analysis of the ester, in such dilute solutions, is obviously very difficult and is complicated by the fact that the solutions decompose so rapidly. Nevertheless, the purest solutions of the ester which were obtained contained approximately two moles of alcohol for each gram atom of chromium, therefore suggesting the formula $(CH_3)_2CHOCrO_2OCH(CH_3)_2$. Furthermore, the fact that the yellow solute in benzene is actually a neutral ester is confirmed by the facts (a) that chromic acid itself cannot be extracted from aqueous solutions into benzene, or into benzene plus acetone, and (b) that the solution of the ester in benzene cannot be extracted into water by washing with aqueous bicarbonate or carbonate solutions.

When a drop of pure, dry pyridine is added to a few milliliters of a solution of the ester in benzene, the ester is instantly destroyed; the solution becomes brown and turbid and acetone is formed. When the concentration of pyridine is 0.001 molar, the decomposition requires fifteen to thirty seconds. A similar decomposition can be accomplished with dimethylaniline or quinoline; diphenylamine (which is a strong reducing agent but a weak base) decomposes the ester only slowly. It is therefore probable that pyridine is functioning as a base.

Qualitative experiments, similar to those here reported for the isopropyl ester of chromic acid, have been carried out with the secondary butyl and borneol esters.

II. Base Catalysis of Chromic Acid Oxidation in Aqueous Solution

Previous experiments[2] on the chromic acid oxidation of isopropyl alcohol suggested that the reaction is second order in hydrogen ion in 0.2–0.5 molar acid, but that it is first order in hydrogen ion in more dilute acid. This has proved to be the fact, and the rate data have been analyzed in terms of two simultaneous reactions

$$d(Cr^{+++})/dt = k_{obs.}(HCrO_4^-)(CH_3CHOHCH_3) \quad (3)$$

where

$$k_{obs.} = k_3(H^+) + k_4(H^+)^2$$

Representative data confirming equation 3 are presented in Table I. For the range of acidity under consideration in the present problem, only the term (in equation 3) involving k_3 is important.

It was here found that, in the presence of pyridine and pyridinium ion, the rate of the chromic acid oxidation of isopropyl alcohol was accelerated, in some cases, by more than 50%. Since the ionization constant of pyridinium ion[8] is about 5×10^{-6}, and since the concentration of acid here used was in the range of 0.003–0.01 molar, the concentration of free pyridine in these solutions was very small (of the order of 0.00005 molar), and therefore the observed effect on the reaction rate shows that pyridine is a very powerful catalyst for the oxidation. The reactions were carried out at 25°, where the ionization constant of pyridine is better known than at 40°. The acceleration in rate here noted was not caused by errors in the calculated concentrations of hydrogen ions (or of other reagents) since the acidity of these solutions was checked by an indicator method.

TABLE I

EFFECT OF ACIDITY ON THE RATE OF CHROMIC ACID OXIDATION OF ISOPROPYL ALCOHOL

$(CrO_3) = 0.00100$ m./l., $CH_3CHOHCH_3 = 0.200$ m./l., $\mu = 0.25$, $T = 40°$

H^+, m./l.	$k_3 = 0.073$ min.$^{-1}$ (m./l.)$^{-2}$ $10^4k_{obsd.}$, min.$^{-1}$ (m./l.)$^{-1}$	$k_4 = 1.66$ min.$^{-1}$ (m./l.)$^{-3}$ $10^4k_{calcd.}$, min.$^{-1}$ (m./l.)$^{-1}$
0.0050	4.4	4.1
.0108	9.8	9.8
.0150	14.8	14.7
.0520	82.8	83.2
.1224	343	338
.2508	1200	1200

TABLE II

THE PYRIDINE CATALYSIS OF THE CHROMIC ACID OXIDATION OF ISOPROPYL ALCOHOL

$(CrO_3) = 0.000200$ m./l., $(CH_3CHOHCH_3) = 0.260$ m./l., $\mu = 0.26$, $T = 25°$

H^+, m./l.	HPy^+, m./l.	10^6Py, m./l.	$10^4k_{obsd.}$, min.$^{-1}$ (m./l.)$^{-1}$
0.0090	...	...	1.62
.0090	0.060	33	1.92
.0090	.190	106	2.33
.0046	...	...	0.591
.0046	.190	206	1.22

Experimental

Materials.—The chromic acid and isopropyl alcohol used in these experiments were purified as in previous work.[3] Mallinckrodt A.R. pyridine was dried over barium oxide and then distilled, with adequate protection from moisture, through a 24″ column packed with single-turn glass helices. It boiled at 115.3 ± 0.1° and had a density,[9] $d^{25}_4 = 0.9778$. It did not decolorize dilute chromic acid in a mixture of perchloric acid and acetic acid, and was therefore free from reducing impurities. The perchloric acid was reagent grade; the sodium perchlorate (used to maintain constant ionic strength) was recrystallized from water and gave a negligible test for chloride ion. Reagent grade, thiophene-free benzene was distilled through an 18″ Podbielniak column; reagent grade toluene was used directly.

Preparation of the Chromic Acid Ester.—Twenty milliliters of 0.1 molar aqueous CrO_3 and 1 ml. of isopropyl alcohol were shaken with 20 ml. of benzene. The benzene layer became yellow at once, and the yellow color deepened as the shaking continued. After 5 minutes, the layers were allowed to separate. The benzene layer was rapidly washed with a 100-ml. portion of cold calcium chloride solution, and then with 100 ml. of cold water; the solution was then dried with calcium chloride. More thorough washing than that

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here described generally results in extensive and prompt decomposition of the ester. Washing with carbonate solution does not result in much more extensive decomposition than does washing with water, presumably because the inorganic base (Na_2CO_3) is insoluble in benzene. The washing is necessary to reduce to a minimum the concentration of free isopropyl alcohol in the benzene layer; for many experiments, the alcohol is not undesirable, and the benzene layer can be dried after only one washing. Since the partition coefficient of isopropyl alcohol between benzene and water[10] is around $^1/_4$ the washing here described reduces the concentration of alcohol in the benzene to about 0.0001 mole/liter. There is also a trace of acetone in the benzene layer. The acetone is formed both during the preparation of the ester and by its decomposition while it is washed. Since the partition coefficient of acetone between water and benzene is of the order of unity,[11] not all the acetone is removed.

If aqueous chromic acid, or aqueous chromic acid containing acetone but no alcohol, is shaken with benzene, the benzene layer remains colorless.

Analysis of the Ester.—Since the ester, even in dilute solution in aromatic solvents, is extremely unstable, the quantitative analyses here reported are necessarily crude. The analysis was conducted as follows: A solution of the ester in toluene was prepared, washed twice with ice-cold 7% calcium chloride solution, and dried. The chromium analysis was conducted by reducing an aliquot of the toluene solution of the ester with aqueous sulfur dioxide. The chromium was quantitatively extracted into the aqueous layer as Cr^{+++}, and was then converted into the complex with ethylenediaminetetraacetic acid.[12] This complex, which is advantageous because it has a high extinction coefficient, was then determined spectrophotometrically with a Beckman model DU-8 quartz spectrophotometer.

The analysis for isopropyl alcohol in the chromic acid ester was accomplished by converting the alcohol (and the acetone formed by decomposition of the ester) to iodoform; the iodoform was determined spectrophotometrically[13] at 3500 Å. The detailed procedure was as follows: A 10-ml. sample of the toluene solution of the ester was decomposed by light, and then refluxed for sixty minutes with an aqueous solution 0.3 molar in I_2, 0.6 molar in KI and 0.4 molar in NaOH. The iodoform produced during the reaction was extracted into the benzene layer; excess iodine was removed by washing the toluene solution with a small amount of aqueous alkali. The toluene solution of iodoform was dried and examined spectrophotometrically; the absence of iodine was demonstrated, since these solutions showed essentially no absorption at 5000 Å. The procedures here outlined were carried out in dim light to avoid the photochemical decomposition[14] of iodoform; the brief exposure to the beam of the spectrophotometer did not cause measurable decomposition. Control experiments gave an average yield of iodoform of 68 ± 5%; acetone gave roughly the same yield as did isopropyl alcohol. The analyses for the isopropyl alcohol in the ester solutions were corrected for the yield of iodoform determined in these control experiments. An additional set of control experiments was performed in which dilute aqueous perchloric acid was substituted for the aqueous chromic acid employed in the preparation of the chromic acid ester. The toluene layer, obtained in these control experiments, contained a dilute solution of isopropyl alcohol; these solutions were washed and analyzed as described above. The results of these experiments showed that a correction (usually amounting to about 10%) had to be subtracted from the amount of iodoform determined spectrophotometrically.

A series of seven experiments with approximately 0.002 molar ester, conducted in the manner here outlined, gave the following values for the ratio of isopropyl alcohol to chromium: 1.80, 1.94, 2.16, 2.03, 2.40, 1.91 and 2.07. The average value is 2.04 ± 0.14. Considering the instability of the ester, the analyses correspond reasonably well to the formula for diisopropyl chromate.

Identification of the Oxidation Product.—The acetone, formed by the pyridine-catalyzed decomposition of a benzene solution of diisopropyl chromate, was isolated and identified as the 2,4-dinitrophenylhydrazone. Twenty-five ml. of a 0.00107 molar solution (chromium analysis) of the ester in benzene was decomposed with pyridine, and the insoluble chromium compounds removed by centrifugation. The clear benzene layer was shaken with a sulfuric acid–water–alcohol solution of 2,4-dinitrophenylhydrazine. When this solution was shaken with pure benzene, the hydrocarbon remained colorless. However, when the solution of decomposed ester was used, acetone 2,4-dinitrophenylhydrazone was extracted into the benzene layer. The benzene was washed, dried and evaporated in vacuum. The residue was redissolved in ether, and the evaporation repeated. The crude residue weighed 7.8 mg.; after two recrystallizations from absolute alcohol it melted at 124–126°; a mixed melting point with an authentic sample of acetone 2,4-dinitrophenylhydrazone showed no depression. The yield of crude acetone 2,4-dinitrophenylhydrazone was 60%, based on diisopropyl chromate. This probably corresponds to one mole of acetone per mole of ester; the fact that the yield somewhat exceeds 50%, may be due either to impurities in the crude derivative, or to air oxidation induced by the decomposition of the chromic acid ester.[15]

An additional test for acetone was conducted colorimetrically. The benzene solution of the decomposed ester was extracted with water, and the acetone estimated with salicylaldehyde.[16] When the test was conducted with an undecomposed solution of the ester, from 10 to 30% as much acetone was found as in the solution of ester decomposed by pyridine. Presumably acetone is formed by the decomposition induced by water; continued washing completely destroys the ester. This decomposition, which necessarily accompanies the washing of the ester, contributes to the inaccuracy of the analysis.

Kinetic Method.—The concentration of chromic acid in aqueous solutions was followed spectrophotometrically.[4] The kinetic equations employed were generally similar to those of Westheimer and Novick[2]; the rate constants here reported are those for the reaction of the acid chromate ion, $HCrO_4^-$. Since in general the concentrations of acid and alcohol were, as a first approximation, unchanged during any particular kinetic experiment, a simple first order equation could be used, and the rate constant corrected for the fact that only a fraction (with 0.001 molar chromate, the fraction is 0.906) of the total hexavalent chromium is present as $HCrO_4^-$. However, in the very dilute acid solutions, some further refinement was necessary. It can be shown[17] that the integrated form of equation (3) may be approximated by (4), where a is the initial concentration of alcohol, b the initial concentration of CrO_3, c the initial concentration of hydrogen ion and x the concentration of Cr^{+++} present at time t.

$$2.303 \log \frac{b}{b-x} + \frac{2Lx^2}{bc} = (k_3'ac + k_4'ac^2)t \quad (4)$$

Equation (4) is valid provided that $c > b$ and $a \gg b$. In this equation, the symbol L is defined by equation (5).

$$L = \frac{1 + 2k_4'c/k'_3}{1 + k_4'c/k'_3} \quad (5)$$

Approximate values of k_3' and k_4' allow an approximation of L; the final values of the constants can then be found by successive approximations. The rate constants k_3 and k_4 differ from k_3' and k_4' respectively, in that the former have been

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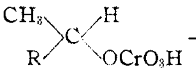
corrected[2] for the fact that only $HCrO_4^-$ is the reactive oxidizing agent.

The acidity of solutions containing perchloric acid was compared to those containing perchloric acid, pyridine and pyridinium ion, using thymol blue as indicator. The method outlined by Brode[18] was used; at a *p*H of 2 the indicator is in its most sensitive range. The acidities of the perchloric acid solutions were identical, within experimental error, with the corresponding solutions containing pyridine; certainly the difference did not exceed 1% of the hydrogen ion concentration.

Conclusions

The objective of the present series of investigations is the elucidation of the mechanisms of chromic acid oxidation in aqueous solution. The ester in benzene is most probably diisopropyl chromate. By contrast, the kinetics of the oxidation in aqueous solution shows that, if the ester mechanism is correct, the intermediate must be monoisopropyl chromate. Since the C–H bond of the alcohol is cleaved in the rate controlling step of the reaction,[4] and since it has here been shown that pyridine catalyzes the reaction in aqueous solution, the mechanism represented by equations (1) and (2) becomes highly probable. Furthermore, a mechanism analogous to that represented by (1) and (2) probably explains the pyridine-catalyzed decomposition of the ester in benzene or toluene solution. (It is possible that the pyridine may also, or in some cases alternatively, complex with the chromium atom of the ester. The mechanism for the reaction in aprotic solvents is not yet completely understood.) The parallel between the decomposition of the ester in benzene and in water is strengthened by the fact that the reaction in aqueous solution[19] as well as that in benzene, can be photochemically accelerated.

The ester mechanism for the chromic acid oxidation of isopropyl alcohol in aqueous solution is consistent with numerous other facts concerning oxidation in polar media. For example, the by-products obtained in the oxidation of methyl-*t*-amylcarbinol[20] may be explained[1,5] by the ester mechanism. The chromic acid ester of this alcohol can decompose by either of two mechanisms; one of these is the normal oxidation to the ketone, analogous to that shown in equations (1) and (2); the other mechanism is represented by equations (6) and (7); where R represents the *t*-amyl group.



$$\mathrm{CH_3(R)C(H)OCrO_3H} \longrightarrow \mathrm{CH_3CHO} + \mathrm{HCrO_3^-} + \mathrm{R^+} \quad (6)$$

$$\mathrm{R^+} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{ROH} + \mathrm{H^+} \quad (7)$$

(The fate of the $HCrO_3^-$, a compound of tetravalent chromium, has been discussed elsewhere.[3,5]) In reaction (6), a solvated *t*-amyl carbonium ion splits from the ester and reacts with water to form *t*-amyl alcohol. This type of by-product will presumably only be formed in those instances where the solvated carbonium ion has reasonable stability, *i. e.*, only where the ion is of the tertiary or benzyl type.[21]

It is pertinent to note that several other oxidizing agents also function by way of esters as intermediates.[22]

Summary

1. A dilute benzene solution of a neutral ester of chromic acid and isopropyl alcohol (presumably diisopropyl chromate) has been prepared.

2. The ester is very unstable; its decomposition is strongly catalyzed by bases such as pyridine.

3. The chromic acid oxidation of isopropyl alcohol in 0.01 molar aqueous acid is also catalyzed by pyridine.

4. These facts, together with those previously known about chromic acid oxidations, indicate that an ester is an essential intermediate in the oxidation of isopropyl alcohol by aqueous chromic acid.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Mechanism of the γ-Ray Induced Oxidation of Formic Acid in Aqueous Solution

BY EDWIN J. HART

Recent work of Allen,[1] Dainton,[2] Krenz,[3] Miller,[4] and Weiss and Stein[5] has given considerable support to the suggestion of Weiss[6] that free hydrogen atoms and hydroxyl radicals are the principal active species liberated in liquid water by ionizing radiation. This present communication reports work on the specific action of the hydroxyl radical in aqueous solutions of formic acid.

According to present concepts hydrogen and hydroxyl radicals are produced in equal numbers during irradiation of water or aqueous solutions with γ-rays. Unless a complete analysis of all reaction products can be made, it is difficult to differentiate between the chemical effects of these two radicals. This is particularly true in solutions containing organic molecules. However, it is found that the effect of the hydroxyl radical can be

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