[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

The Chemistry of Diisopropyl Chromate

By Albert Leo and F. H. Westheimer

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Depending upon the experimental conditions, diisopropyl chromate in benzene solution can undergo either hydrolysis or internal oxidation–reduction. The rate of the latter reaction is approximately first order in pyridine and first order in the chromic acid ester, but is decreased by added isopropyl alcohol. The chromic acid ester of 2-deuteropropanol-2 undergoes internal oxidation–reduction only about a fifth as fast as does that of isopropyl alcohol. Further, the (Oppenauer) reaction, which employs di-*t*-butyl chromate as an oxidizing agent, resembles the internal oxidation–reduction reaction in that both are accelerated by pyridine. These facts are correlated with the ester mechanism for chromic acid oxidations.

Introduction

It has recently been shown[1,2] that monoisopropyl chromate is probably an intermediate in the chromic acid oxidation of isopropyl alcohol in aqueous solution. Diisopropyl chromate can be prepared as a dilute solution in benzene[1]; in the present paper, the kinetics and mechanism of the decomposition of this and other chromic acid esters are discussed.

Experimental

2-Deuteropropanol-2.—Westheimer and Nicolaides[3] prepared an isotopically impure sample of 2-deuteropropanol-2 by the catalytic deuteration of acetone. To prepare isotopically pure 2-deuteropropanol-2, thirty grams of acetone was reduced with four grams of lithium aluminum deuteride (Metal Hydrides Co.) suspended in 150 cc. of dry ether. (Samples of $LiAlD_4$, more recently purchased from Metal Hydrides, completely dissolved in ether.) The reaction was conducted under nitrogen, following the technique for lithium aluminum hydride reductions.[4] When the reaction was complete, the mixture was treated with 430 cc. of six per cent. sulfuric acid. The heterogeneous reaction mixture was fractionated through an 18″ Podbielniak column, at a reflux ratio of 25 to 1. The azeotrope (17.4 g.) which boiled at 79.0–80.5°, was refluxed over calcium oxide and the dry alcohol distilled through a small tantalum-wire column. The fraction (12.1 g. or 53% of theory) boiling at 82.2° (750 mm.) was pure 2-deuteropropanol-2.

In order to analyze the compound for deuterium, it was diluted with a known quantity of dry isopropyl alcohol, the mixture burned, and the water collected. This water was analyzed both by the float technique[3,5] and by converting the water to a hydrogen–deuterium mixture, and analyzing the gas with a Consolidated Nier isotope-ratio type mass spectrometer.[6] Found: Float method, 11.8 atom per cent. deuterium, mass-spectrometric method, 12.7 atom per cent. deuterium; calcd.: 12.5 atom per cent. deuterium.

To determine whether exchange with the methyl groups of acetone had accompanied reduction, the 2-deuteropropanol-2 was oxidized to acetone by the Oppenauer method with fluorenone and aluminum *t*-butoxide.[3,7] The acetone was isolated as the 2,4-dinitrophenylhydrazone, diluted with a known amount of ordinary acetone 2,4-dinitrophenylhydrazone, and analyzed for deuterium. Two measurements (mass-spectrometer method) showed no excess deuterium in the derivative.

Diisopropyl Chromate.—The preparation of solutions of this ester in benzene or toluene has previously been described.[1] An alternative method (which has the advantage of avoiding water) consists in shaking a benzene solution of isopropyl alcohol with a few crystals of solid CrO_3. The concentration of ester so formed can be determined either by analyzing the solution for total chromium, or by spectrophotometric analysis for the ester.

Di-*t*-butyl Chromate.—Solutions of di-*t*-butyl chromate in benzene can be made by either of the methods used for the preparation of diisopropyl chromate. H. Wienhaus[8] had previously prepared this compound as an oil; the compound may be prepared in solid form as follows: A solution of 1.5 g. of *t*-butyl alcohol in 50 cc. of purified ligroin is shaken with 1.0 g. of dry CrO_3. The solution is decanted onto calcium chloride, filtered, and then cooled in Dry Ice. The red crystals which separate are decanted, and recrystallized from ligroin; they melt at about −5 to 0°. On analysis, the compound was shown to contain two molecules of *t*-butyl alcohol for each atom of chromium; recrystallization of the crystals from ligroin containing 10% *t*-butyl alcohol gave material which had the same analysis.

Analysis for Chromium.—A weighed portion of the crystalline solid was dissolved in 20 cc. of benzene, and the solution decomposed with 3 cc. of an aqueous solution of SO_2. The liquids were separated, and the aqueous layer again extracted with benzene, in order to extract from it almost all the *t*-butyl alcohol. The trivalent chromium in the aqueous solution was then converted to its ethylenediamine tetraacetic acid complex, and estimated[1,9] spectrophotometrically. From this analysis and the optical density of the ester in benzene, the extinction coefficient of the ester at 3500 Å. was found to be 2480.

Analysis for *t*-Butyl Alcohol.—The analysis of *t*-butyl alcohol in the benzene solution was carried out by an empirical method which makes use of the fact that di-*t*-butyl chromate has a very high extinction coefficient. The benzene solution in question is transferred to a separatory funnel and mechanically shaken for five minutes with a few drops of a 50% aqueous solution of CrO_3. The benzene layer is then washed with two 25-cc. portions of water, dried with calcium chloride, and filtered; the concentration of the ester is determined spectrophotometrically. Control experiments showed that the quantity of ester formed in this procedure does not depend upon the exact amount of the aqueous chromic acid used, or on the time of shaking (beyond five minutes). On the other hand, the yield of ester is by no means quantitative, nor can a value for the equilibrium constant for the formation of di-*t*-butyl chromate be obtained from the data. The method was therefore calibrated with benzene solutions of known concentrations of *t*-butyl alcohol. For the range of *t*-butyl alcohol concentrations between 2×10^{-4} and 4×10^{-3} mole/liter, the reproduci-

Table I

Empirical Standardization for Analysis of *t*-Butyl Alcohol in Benzene

Concn. *t*-butyl alcohol added, mole/liter × 10^4	Optical density, 3500 Å.	Concn. ester, found mole/liter × 10^4
4.5	0.124	0.50
8.1	.211	0.85
9.3	.235	0.95
11.1	.288	1.15
12.9	.327	1.32
18.6	.496	2.00
33.2	.837	3.38
37.2	.945	3.81

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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); Errata, June, 1950.

[3] F. Westheimer and N. Nicolaides, This Journal, **71**, 25 (1949).

[4] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

[5] W. G. Brown and K. Eberly, This Journal, **62**, 113 (1940).

[6] R. Alfin-Slater, S. M. Rock and M. Swislocki, *Anal. Chem.*, **22**, 421 (1950).

[7] R. Baker and H. Adkins, This Journal, **62**, 3305 (1940).

[8] H. Wienhaus and W. Treibs, *Ber.*, **56**, 1648 (1923).

[9] G. Schwartzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948).

bility of the method was better than ±5%. The pertinent data are assembled in Table I.

Other Materials.—Thiophene-free benzene was purified by refluxing it with solid CrO_3, and then fractionating the solvent at atmospheric pressure. Other chemicals were reagent grade.

Oxidation of Benzyl Alcohol.—When a mixture of 44.4 g. of *t*-butyl alcohol and 20 g. of CrO_3 in 70 cc. of benzene was added to 16.2 g. of benzyl alcohol and 1 cc. of pyridine, a 70% yield of benzaldehyde was obtained three-quarters of an hour after the addition was begun. (The reaction was stopped at this time by the addition of excess of hydrazine sulfate.) The same reaction in the absence of pyridine gave only a 55% yield of benzaldehyde after three hours of reaction. The difference in reaction rate was also apparent in the greater amount of heat developed in the catalyzed reaction.

Kinetic Method.—As the decomposition of diisopropyl chromate in benzene proceeds, the reduced form of the chromium compound appears as a brown turbidity. (On analysis, this solid was found to contain 42% Cr^6 and 58% Cr^3; it therefore contains somewhat more Cr^6 than would correspond to CrO_2.) It was found possible to follow the appearance of this brown turbidity by spectrophotometric measurements at 6000 Å. Careful standardization showed, somewhat unexpectedly, that the brown solid obeys Beer's law, provided the measurements are made within half an hour. After long periods of elapsed time, the brown solid settles in the spectrophotometer tube; even then, readings of moderate reliability can be obtained if the solid is again suspended, by vigorous shaking, in the benzene.

Standardization.—Diisopropyl chromate was prepared, and its optical density measured. Then the rate of pyridine catalyzed decomposition was followed (a) by the increase with time in optical density at 6000 Å., and (b) by removing samples of the reaction mixture from time to time, centrifuging them rapidly, and determining spectrophotometrically the residual concentration of ester in the filtrate. The two methods agreed when an extinction coefficient of 410 was assigned to the brown solid. A typical set of data is shown in Fig. 1. The method is limited to those reaction mixtures where reaction occurs rapidly, and where the optical density does not exceed 0.5. However, most of the reactions here described are very rapid; under these circumstances, the method is not only more convenient but actually more precise than one which requires a filtration prior to the spectrophotometric determination.

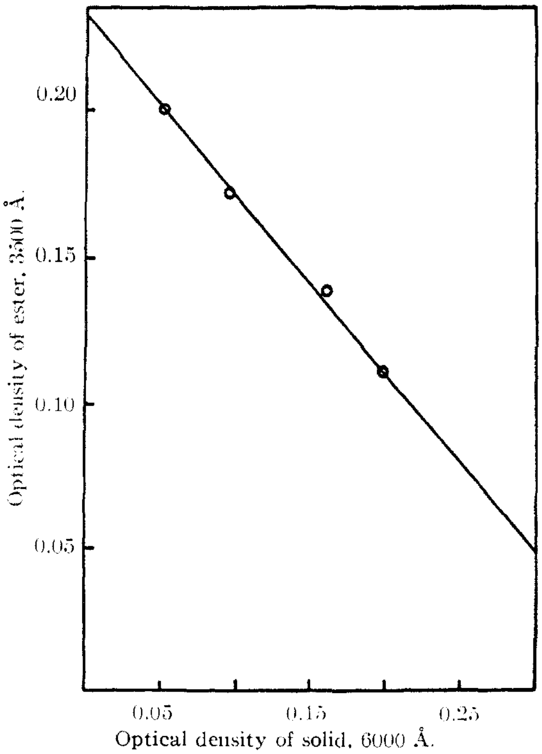

Fig. 1.—Standardization of analytical method.

Oxygen Effect.—W. A. Waters has shown[10] that some chromic acid oxidations are profoundly affected by the presence of oxygen. Therefore the rate of decomposition of diisopropyl chromate was measured in the absence of air. A solution of the ester and excess alcohol in benzene was placed in one arm of an inverted U-tube, and a solution of pyridine in benzene in the other. To one end of the U-tube, a piece of optically-polished square Pyrex tubing had been sealed; this tubing served as a spectrophotometer cell. Both solutions were degassed twice on the vacuum line, the system sealed and then the solutions mixed. The rate of decomposition was then followed spectrophotometrically; about 20% of the diisopropyl chromate had decomposed before the first spectrophotometric observation was made.

Results

Di-*t*-butyl Chromate.—The decomposition of a solution of crystallized di-*t*-butyl chromate at room temperature in pure, dry benzene requires several days. Even in the presence of 0.001 molar pyridine, a 0.001 molar solution of the ester was unchanged after 30 minutes. However, in the presence of a trace (0.005 mole/liter) of water, the ester rapidly hydrolyzes; the hydrolysis is strongly catalyzed by pyridine (R = *t*-butyl).

$$ROCrO_2OR + H_2O \rightleftarrows CrO_3 + 2ROH \qquad (1a)$$

$$CrO_3 + H_2O + C_5H_5N \leftrightarrows C_5H_5NH\ HCrO_4 \qquad (1b)$$

The products formed were estimated as follows: The solution was filtered, and the yellow solid (which had formed during the reaction) was dissolved in dilute aqueous perchloric acid. It was analyzed for hexavalent chromium spectrophotometrically, at 3500 Å. The solution was then treated with ethylenediaminetetraacetic acid in an acetate buffer, and analyzed for trivalent chromium; there was less than 0.3% of the latter present. The yellow solid was identified as pyridinium acid chromate by chromium and nitrogen analysis. The *t*-butyl alcohol, determined by the empirical method already outlined, corresponded in quantity to two moles for each mole of ester used, or of hexavalent chromium compound precipitated.

No accurate kinetics for the hydrolysis of di-*t*-butyl chromate were obtained. However, the rate is increased by increasing concentrations of water and of pyridine, and strongly decreased by added *t*-butyl alcohol. In the presence of 0.5 *M* *t*-butyl alcohol and 0.001 *M* pyridine, a 0.001 *M* solution of the ester was essentially unchanged after 12 hours.

Diisopropyl Chromate. (a) Internal Oxidation–Reduction.—Diisopropyl chromate in benzene can undergo two competitive reactions: hydrolysis and internal oxidation–reduction. The hydrolysis is represented by equation (1) where R is isopropyl; the oxidation–reduction is represented by equation (2).

$$(CH_3)_2CHOCrO_2OCH(CH_3)_2 \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH + CrO_2 \qquad (2)$$

Both reactions are accelerated by pyridine; the hydrolysis is much more strongly retarded by excess isopropyl alcohol than is the oxidation–reduction. In the strict absence of water, the rate of the internal oxidation–reduction reaction of diisopropyl chromate is approximately first order in pyridine concentration and ester concentration, and is an ap-

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

proximately linear inverse function (see Fig. 2 and equation 5) of the isopropyl alcohol concentration.

TABLE II

RATE OF INTERNAL OXIDATION–REDUCTION OF DIISOPROPYL CHROMATE IN DRY BENZENE AT 25°

Concentrations, m./l.

$(i\text{-Pr})_2CrO_4$ × 10^4	i-PrOH	"Gross" Py × 10^4	"Free" Py × 10^4 (Eq. 4)	$10^2k_{obsd.}$, min.$^{-1}$	Rate constants k_2, min.$^{-1}$ (m./l.)$^{-1}$ calcd. by eq. 4–6
3.4	...	4.0	4.0	13	330
3.6	0.068	4.0	1.8	6	340
4.1	.068	4.0	1.8	6	330
4.1	.250	4.0	0.73	2.6	360
3.1	.41	4.0	.48	1.5	320
4.0	.52	3.9	.38	1.3	340[a]
4.6	.670	4.0	.31	1.1	350
0.11	.12	4.0	1.26	5.8	460
0.53	.12	4.0	1.26	7.7	480
1.06	.12	4.0	1.26	8.2	540
4.0	.57	70	6.5	28	420
4.0	.57	38	3.4	13	320
4.0	.57	3.8	0.34	1.5	450

[a] Experiment in vacuum.

(b) **Hydrolysis.**—When diisopropyl chromate and pyridine are dissolved in wet benzene, both hydrolysis and internal oxidation–reduction occur. If the concentration of alcohol is low, the over-all reaction consists essentially of hydrolysis; the reaction proceeds about ten times as fast in wet benzene as does the corresponding oxidation–reduction in dry benzene. The constants in Table III have been calculated on the assumption that the reaction is first order in ester, in water and in gross pyridine concentrations.

TABLE III

HYDROLYSIS OF DIISOPROPYL CHROMATE IN BENZENE SOLUTION AT 25°

Concentrations, m./l.

$(i\text{-Pr})_2CrO_4$ × 10^4	"Gross" Py × 10^4	H_2O, × 10^4	CrO_3 in product, %	Approx. k × 10^5, min.$^{-1}$ (m./l.)$^{-2}$
4.7	4.0	125	90	5.6
3.2	2.8	45	94	4.8

Isotopic Alcohols.—In dry benzene, and in the presence of excess 2-deuteropropanol-2, the rate of decomposition of the chromic acid ester of 2-deuteropropanol-2 is about a fifth that of the ester of ordinary isopropyl alcohol (Table IV). When the alcohol-free ester of the deutero alcohol is decomposed by pyridine in wet benzene, the rate of hydrolysis is approximately the same as that for the ester of ordinary isopropyl alcohol. Since, however, the rates of the hydrolysis reactions are large, and were not accurately measured, no quantitative comparison of these rates of hydrolysis is here offered.

TABLE IV

RELATIVE RATES OF DECOMPOSITION OF CHROMIC ACID ESTERS OF ISOPROPYL ALCOHOL AND OF 2-DEUTEROPROPANOL-2

	Concentrations, m./l.			Rate constants	
Ester	$(i\text{-Pr})_2$ CrO_4 × 10^4	i-PrOH × 10^4	"Gross" Py × 10^4	10^2 $k_{obsd.}$, min.$^{-1}$	Rel. rate const.
2-Propyl	3.6	0.12	4.5	5.0	100
2-Deutero-2-propyl	5.0	.12	4.5	1.03	21
	10.6	.13	4.0	0.96	19
	106	.13	4.0	1.24	25
	106	.24	4.0	1.10	22

Ester Exchange.—In the presence of 2-deuteropropanol-2, diisopropyl chromate is slowly decomposed, whereas in the presence of ordinary isopropyl alcohol, the ester of the deuteroalcohol is rapidly decomposed. Further, di-*t*-butyl chromate (which undergoes only very slow decomposition when dissolved in pure, dry benzene) oxidizes isopropyl alcohol at a rate comparable to the rate of decomposition of the ester of the secondary alcohol. It seems improbable that this oxidation proceeds by way of a bimolecular reaction between di-*t*-butyl chromate and isopropyl alcohol, since the rate of the oxidation decreases with increasing concentration of isopropyl alcohol, just as does the rate of the internal oxidation–reduction of diisopropyl chromate. Presumably in all these reactions, ester exchange occurs, and the reaction is essentially that of the chromic acid ester of the alcohol present in large excess.

TABLE V

ESTER EXCHANGE[a]

Ester	Concentrations, m./l.				$10^2k_{obsd.}$, min.$^{-1}$
	Ester × 10^4	i-PrOH	D-i-PrOH	t-BuOH	
$(i\text{-Pr})_2CrO_4$	4.9	0.12	..	...	5.9
$(i\text{-Pr})_2CrO_4$	5.5	0.12	..	...	6.2
$(i\text{-Pr})_2CrO_4$	4.9	...	0.12	...	2.5
$(i\text{-Pr})_2CrO_4$	5.5	...	0.12	...	2.1
$(i\text{-Pr})_2CrO_4$	4.9	0.11	..	...	5.7
$(i\text{-Pr})_2CrO_4$	3.4	.013	..	0.097	0.4
$(i\text{-Pr})_2CrO_4$	3.6	.013	..	.097	0.3
$(t\text{-Bu})_2CrO_4$	3.9	.12	..	...	1.5
$(t\text{-Bu})_2CrO_4$	4.1	...	..	.10	Too small to measure

[a] Gross Py = 4 × 10^{-4} m./l.

Oppenauer Di-*t*-butyl Chromate Oxidation.—Recently Oppenauer[11] has shown that di-*t*-butyl chromate in benzene solution can act as an oxidizing agent. For those reactions in which the reducing agent is an alcohol, ester exchange offers a plausible reaction scheme. In conformity with this proposal, it has been shown that pyridine catalyzes the oxidation of benzyl alcohol by di-*t*-butyl chromate.

Discussion

Since the reaction rate for the internal oxidation–reduction of diisopropyl chromate is first order in pyridine, and since the rate is much slower for the chromic acid ester of 2-deuteropropanol-2 than for the corresponding ester of isopropyl alcohol, it is probable that a base removes a proton from the ester in the rate-controlling step of the reaction

$$(CH_3)_2CHOCrO_2R + B \longrightarrow BH^+ + (CH_3)_2CO + ROH + CrO_2 \quad (3)$$

The reaction in benzene thus closely parallels that in water. In aqueous solution, R is a hydrogen atom and the compound of tetravalent chromium produced in the rate controlling step reacts further; in benzene solution, where R is an isopropyl

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[11] R. Oppenauer and H. Oberrauch, *Anals. Asoc. quim argentina*, **37**, 246 (1949).

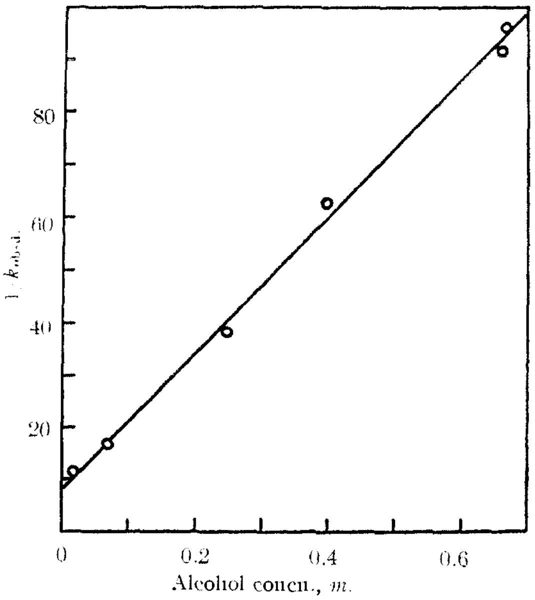

Fig. 2.—Graphical representation of the data of Table II (see equation 5).

group, a compound approaching CrO_2 in composition is precipitated from the solution. A reversible hydrolysis–esterification equilibrium (equation 1) will explain the fact that, in the presence of excess isopropyl alcohol, oxidation–reduction is favored over hydrolysis. However, the fact that the rate of the oxidation-reduction is slowed tenfold in the presence of 0.5 molar isopropyl alcohol certainly requires explanation. A tentative hypothesis which can account for the observations depends upon the fact that, in benzene solution, pyridine is hydrogen bonded by alcohols.[12] If it is assumed that

$$\frac{(\text{Complex})}{(\text{Pyridine})(\text{Isopropyl alcohol})} = K \qquad (4)$$

and that only the "free" (uncomplexed) pyridine is catalytically active (for either hydrolysis or oxidation–reduction) then, for those solutions where the concentration of isopropyl alcohol is large compared to the concentration of pyridine

$$1/k = 1/k_{\text{obsd.}} + Kc/k \qquad (5)$$

where k is the first order rate constant for the decomposition of diisopropyl chromate in benzene solution (in the absence of isopropyl alcohol and at a particular "gross" pyridine concentration), $k_{\text{obsd.}}$ is the corresponding rate constant in the presence of isopropyl alcohol and c is the concentration (in moles/liter) of isopropyl alcohol. That equation (5) is approximately valid is shown in Fig. 2, and by the data of Table I. From Fig. 2, the value of K can be estimated as 18 (moles/liter)$^{-1}$. This value is a reasonable one for the equilibrium in question.[13] The bimolecular rate constants of Table II were calculated from equation (6)

$$k_2 = \frac{k}{(\text{Py})_{\text{gross}}} = \frac{k_{\text{obsd}}}{(\text{Py})_{\text{free}}} \qquad (6)$$

The data of Table II show that as a rough first approximation, the rate of the decomposition of diisopropyl chromate in benzene is represented by equation (7)

$$-\frac{d(\text{Ester})}{dt} = k_2(\text{Ester})(\text{Py})_{\text{free}} \qquad (7)$$

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[12] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939); W. Gordy and S. Stanford, *ibid.*, **8**, 170 (1940).

[13] E. Lassettre, *Chem. Revs.*, **20**, 259 (1937).