coefficients. However, it is found empirically that K'_2/α is independent of concentration within experimental error, having the value 68 (mean deviation ±7). One may therefore conclude with sufficient accuracy that $K_2 \approx 68$.

A similar calculation based on the two rough equilibrium constants determined at 0° is obviously far less significant. The result obtained is that $K_2 \approx 140$ indicating that the reaction of RCl with Br^- is endothermic.

Relative Reactivities.—The constants given in Table V indicate, as has been found in all previously reported cases, that the ion is considerably more reactive than the undissociated salt. The relatively large values for k_m found in the RCl + LiBr system seem to be significantly larger than zero, while in the RBr + LiBr system k_m appears to be indistinguishable from zero. Since the exchange reaction involves a nucleophilic attack on the carbon of the organic halide to which the halogen is bonded, it is entirely reasonable that the charged ion should more readily approach the positive end of the carbon–halogen dipole.

From the equilibrium constants evaluated in the preceding section we may conclude that for the reaction of RBr with Cl^-, k_i is 4.8×10^{-2} at 30° and approximately 1.8×10^{-3} at 0°. Thus at both temperatures the attack of Cl^- on RBr is roughly one-fifth as fast as that of Br^- on RBr, whereas the attack of Br^- on RBr is 310 times as fast as that of Br^- on RCl at 30°, and 800 times as fast at 0°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

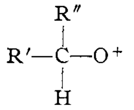
Effect of Nuclear Substitution on the Rate of Oxidation of α-Phenylethanol by Chromium Trioxide[1a]

BY HAROLD KWART AND PETER S. FRANCIS[1b]

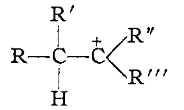
RECEIVED MARCH 9, 1955

A series of *meta* and *para* substituted α-phenylethanols have been synthesized and their rates of oxidation by hexavalent chromium have been determined under acidic and basic conditions and in benzene without catalysts. Application of the data obtained to the Hammett equation gave negative reaction (ρ) constants varying from −0.37 to −1.01 for a variety of reaction conditions. Evidence is presented which suggests that the ρ constants observed in the acid- and base-catalyzed reactions are the sum of a ρ of oxidation and a ρ due to substituent activity in the initial esterification step of the reaction: X-ArRCHOH + $CrO_3 \rightleftarrows$ X-ArRCHOCrO$_3$H.

There have been in recent years several investigations of the mechanism of oxidation of secondary alcohols by chromic acid.[2-4] The results of most of these studies lead to a mechanistic picture closely akin to the elimination reaction.[5] Mosher and coworkers have demonstrated the occurrence of cleavage products in chromate oxidation reactions under common conditions, particularly when the residual cleavage fragment has a tertiary carbon center. This occurrence is strikingly similar to numerous observations of the dehydration reaction, where the carbinol carbon is believed to sustain a large positive charge in the transition state. The suggested analogy of the respective intermediates may be represented as

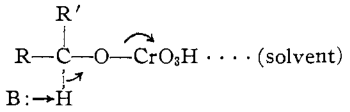


Oxidation

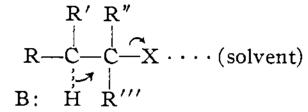


Dehydration (E_1)

Further similarity of the chromate oxidation reaction to the elimination reaction is found in the significant studies of base-catalyzed decomposition of chromate esters as reported by Westheimer and coworkers.[2c,d] Here again the analogous behavior of alcohols (as chromate ester) and halides may be explained in the terms of a common elimination mechanism



Oxidation



Elimination (E_2)

Cristol and co-workers[6] have observed large and positive Hammett ρ[7] values for the base-catalyzed dehydrochlorination of substituted DDT's, indicating the rate-enhancing effects of electron-withdrawing groups in the E_2 reaction.

The foregoing deductions led to the work reported in this communication. A series of *meta* and *para* substituted α-phenylethanols were prepared and their rates of oxidation by hexavalent chromium were measured under widely varying conditions of solvent and catalysis. The purpose of these experiments was to seek further information concerning the mechanism of the reaction.

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(1) (a) Presented in part before the 126th Meeting of the American Chem. Soc., New York, N. Y., Sept., 1954; (b) Walter G. Karr Fellow of Smith, Kline and French Laboratories, 1953–1954.

(2) (a) F. Westheimer, *et al.*, *J. Chem. Phys.*, **11**, 506 (1943); (b) **17**, 61 (1949); (c) THIS JOURNAL, **73**, 65 (1951); (d) **74**, 4383 (1952); (e) **74**, 4387 (1952).

(3) H. G. Kuivila and W. J. Becker, III, *ibid.*, **74**, 5329 (1952).

(4) (a) W. A. Mosher, *et al.*, *ibid.*, **70**, 2544 (1948); (b) **71**, 286 (1949); (c) **73**, 1302 (1951); (d) **72**, 4452 (1950).

(5) Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(6) (a) S. J. Cristol, THIS JOURNAL, **67**, 1494 (1945); (b) S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, *ibid.*, **74**, 3333 (1952).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

Table I summarizes the data obtained for chromic acid oxidation under conditions of acidic, basic and neutral solutions at 30°. The logarithms of the various rate constants have been plotted *vs.* the Hammett[7] σ-constants for the respective substituents and the curves obtained are illustrated in Figs. 1, 2 and 3. The negative values of the slopes in each case were not, at first glance, the type of results expected on the basis of a rate-determining step analogous to E_2 elimination.

TABLE I

RATES OF OXIDATION OF SUBSTITUTED α-PHENYLETHANOLS BY CHROMIC ACID UNDER VARIOUS CONDITIONS

Substituent	k_2, mole^{-1} l.$^{-1}$ min.$^{-1}$ Condition[a] A	Condition[a] B	k_1, min.$^{-1}$ Condition C
p-OCH_3	2.13	1.24	0.0783
p-t-C_4H_9	1.38	...	.0767
p-CH_3	1.06	0.816	.0670
p-H	0.802	.630	.0546
p-Cl	.612	.595	.0355
m-Br	.394	.485	.0426
p-NO_2	.160	.409	.0219

[a] Condition A: 30% acetic acid solvent, $t = 30.1 \pm 0.05°$, $H^+ = 0.250$ *M* (perchloric acid), $\mu = 0.40$ (sodium perchlorate added as needed), $\rho = -1.01$; condition B: 40% pyridine–60% benzene solvent, $t = 30.1 \pm 0.05°$, starting alcohol concentration is 0.04 *M*, $\rho = -0.37$; condition C: benzene solvent, $t = 29.7 \pm 0.05°$, no acid or base catalyst present. The rate constants are for the decomposition of the chromate esters of substituted α-phenylethanols (Cr^{+6} added as 2-(p-nitrophenyl)-2-propanol ester of chromic acid), $\rho = -0.52$.

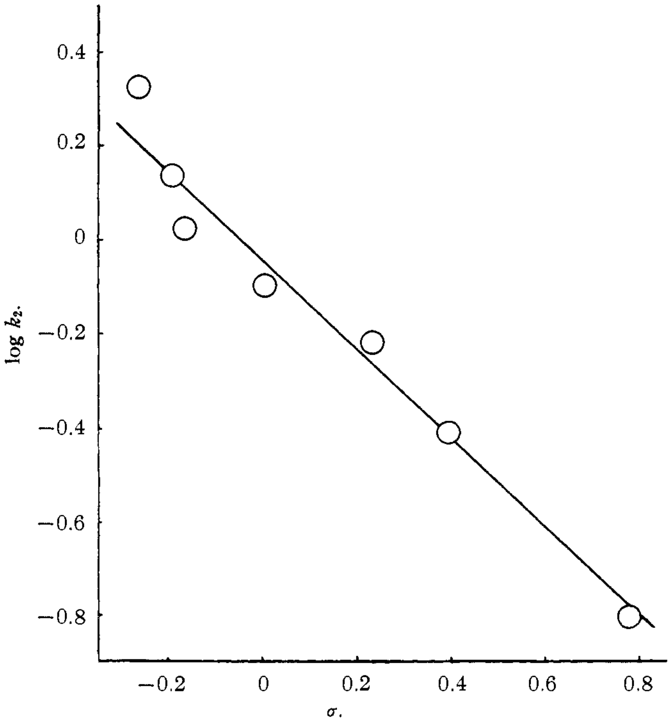


Fig. 1.—Plot of log k_2 *vs.* the Hammett σ-constant for the data in Table I-A (aqueous acetic acid solvent at 30°, with hydrogen ion catalysis). The ρ for this reaction is −1.01.

The Substituent Influence on the Esterification Step.—One very attractive explanation for the data presented can be found in Westheimer's proposals of a chromic ester intermediate

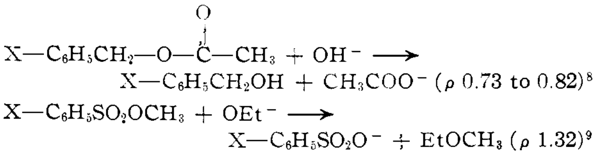
$$HCrO_4^- + ROH + H^+ \underset{k_{-1a}}{\overset{k_{1a}}{\rightleftarrows}} RO{-}CrO_2{-}OH + H_2O$$

and a similar course of reaction may be written for the case of the pyridine–benzene solvent

$$CrO_3 \cdot P_y + ROH \underset{k_{-1b}}{\overset{k_{1b}}{\rightleftarrows}} RO{-}CrO_2{-}OH \cdot Py$$

Some additional evidence for an ester equilibrium of this nature in acid solution will be discussed in a later section of this report. A search of the literature revealed no studies to permit a prediction of the effect of substitution in α-phenylethanols on the forward (k_{1a} and k_{1b}) reactions in these equilibria.

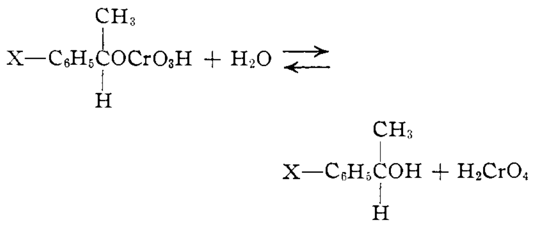
Some experiments have been reported which suggest that substituent effects may be in operation in the reverse (k_{-1a} and k_{-1b}) of the esterification reaction. Below are two of the more striking examples



$$X{-}C_6H_5CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + OH^- \longrightarrow X{-}C_6H_5CH_2OH + CH_3COO^- \ (\rho\ 0.73 \text{ to } 0.82)^8$$

$$X{-}C_6H_5SO_2OCH_3 + OEt^- \longrightarrow X{-}C_6H_5SO_2O^- + EtOCH_3 \ (\rho\ 1.32)^9$$

It is not difficult to visualize the analogous reaction in chromate ester having a ρ-value of similar sign and magnitude



$$X{-}C_6H_5\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}OCrO_3H + H_2O \rightleftarrows X{-}C_6H_5\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}OH + H_2CrO_4$$

The cleavage of the chromium–oxygen rather than the carbon–oxygen bond has been shown recently to be the general course of this type of reaction.[10]

Conceivably, the reverse of the esterification step could not only control the equilibrium concentration of ester in the rate equation of the Westheimer mechanism but also could determine the over-all character of the oxidation ρ. The negative ρ values we are reporting for esterification manifestly could swamp the positive ρ expected on the basis of an E_2 elimination mechanism for decomposition of the chromic ester intermediate. The following experiments were performed in the attempt to establish the existence of this effect tending to overweight the expected positive ρ and produce the observed (over-all) negative ρ.

The chromate diester of α-(p-chlorophenyl)-ethanol in benzene solvent without catalysis has a

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(8) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

(9) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(10) M. Anbar, I. Dostrovsky, D. Samuel and A. D. Yoffe, *J. Chem. Soc.*, 3603 (1954).

half-life of approximately 19 minutes at 30°, decomposing to give one mole of the secondary alcohol, one mole of the corresponding ketone and an insoluble complex compound of chromium.[11] If a solution of the secondary diester is treated with a substituted 2-phenyl-2-propanol the rate of decomposition diminishes rapidly. Also, the nature of the substituent was found to be significant in determining the concentration of tertiary alcohol required to reduce the rate of decomposition to a given extent. This is at once apparent from the data listed in Table II.

We have interpreted the observations listed in Table II as consistent with the ester interchange picture (as discussed by Westheimer and co-workers[2]) and represented by the equation

$$(\text{X—TO})_2\text{CrO}_2 + p\text{=Cl—SOH} \rightleftarrows p\text{-Cl—SOCrO}_2\text{OT—X} + \text{X—TOH} \quad \text{(A)}$$

where X-TOH is a substituted 2-phenylpropanol-2; and p-Cl·SOH is α-(p-chlorophenyl)-ethanol and the equilibrium constant

$$K_{\text{eq}} = [p\text{-Cl—SOCrO}_2\text{OT—X}][\text{X—TOH}]/[(\text{X—TO})_2\text{CrO}_2][p\text{-Cl—SOH}]$$

The rate of decomposition of the chromate ester was taken as a measure of the position of equilibrium. A set of data for substituted tertiary alcohols is presented in Table III and the results are applied to the Hammett equation in Fig. 4. The method for treatment of these data is discussed in the appendix. The K_{eq} values are based on (1) the experimental decomposition rate (k_d = 3.6 $\times 10^{-2}$ min.$^{-1}$) of the disecondary ester (p-Cl-SO)$_2$-CrO$_2$, and (2) the probable[12] decomposition rate (k_d = 1.8 $\times 10^{-2}$ min.$^{-1}$) of the secondary–tertiary ester assumed to be, according to the mechanism above, the reactive component in the solution.

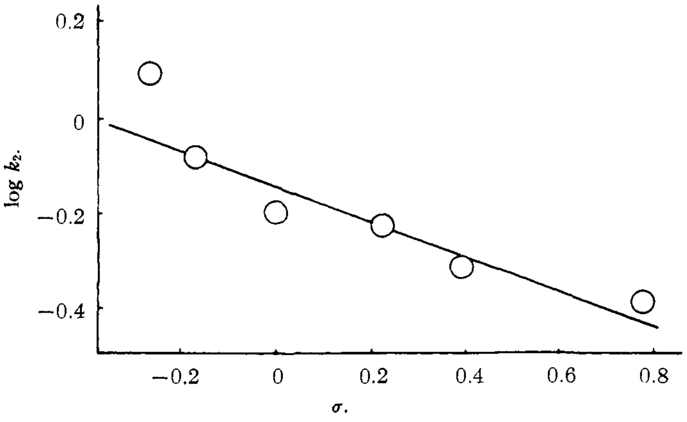

Fig. 2.—Plot of log k_2 against the Hammett σ-constant for the data in Table I-B (pyridine-benzene solvent at 30°, base catalyzed reaction). The ρ of this reaction is −0.37.

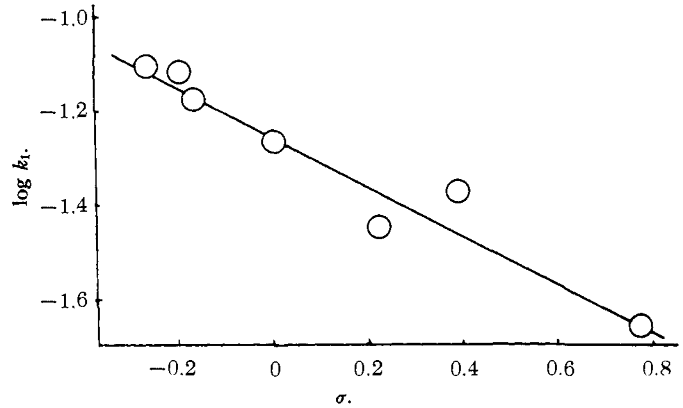

Fig. 3.—Plot of log k_1 *vs.* the Hammett σ-constant for the data in Table I-C (uncatalyzed benzene solvent at 30°). The ρ of this reaction is −0.52.

TABLE II

CONCENTRATIONS OF SUBSTITUTED 2-PHENYL-2-PROPANOL REQUIRED TO EXTEND THE HALF-LIFE OF DECOMPOSITION OF DI-α-(p-CHLOROPHENYL)-ETHYL CHROMATE FROM 19 MINUTES TO *ca.* 80 MINUTES IN BENZENE WITHOUT CATALYSIS

[Cr^{+6}] ~ 0.01 *M*, [α-(p-chlorophenyl)-ethanol] = 0.025 *M*

Substituent	Molar concn. of tertiary alcohol required
p-t-C$_4$H$_9$	0.05
p-CH$_3$	.07
p-H	.10
p-Cl	.20
m-Br	.20
p-NO$_2$	.30

The data in Table IV are the result of a short study designed to determine whether a tertiary alcohol would inhibit the rate of oxidation of α-(p-nitrophenyl)-ethanol by forming its ester with Cr^{+6} in solution and thereby reducing the "activity" of the oxidation solution as shown in the equation

$$\text{HCrO}_4^- + t\text{-C}_4\text{H}_9\text{OH} \rightleftarrows t\text{-C}_4\text{H}_9\text{OCrO}_3^- + \text{H}_2\text{O}$$

Since the kinetics of oxidation in 86.5% acetic acid are first order in Cr^{+6} and first order in isopropyl alcohol,[2e] we must assume the concentration of es-

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

[12] A statistical factor of two was employed, observing that the secondary–tertiary ester has only one decomposable moiety while the disecondary ester has two. The two rate-constants are only approximations since in preparing solutions in which equilibrium is preponderantly in favor of the disecondary ester a small amount of the p-nitro derivative of 2-phenyl-2-propanol was present (see Table V). This treatment seemed quite adequate for determining a ρ-constant of ester equilibrium since the two values used for rate constants of decomposition give only small changes in the slope of the Hammett plot for the equilibrium constants. One other consideration was observed in the determination of these data. The concentration of substituted tertiary alcohol was adjusted in each case so that the rates of decomposition were all within a range of 70–90 minutes half-life. It was thought that the concentration of secondary–tertiary ester should be kept constant since there is without a doubt a side reaction of this ester with more secondary alcohol to give appreciable amounts of disecondary ester according to the equation

$$\text{X—TOCrO}_2\text{OS—}p\text{-Cl} + p\text{-Cl—SOH} \rightleftarrows (p\text{-Cl—SO})_2\text{CrO}_2 + \text{X—TOH}$$

This reaction would have been extremely difficult to include in the rate and equilibrium expressions used and it therefore seemed best to adjust the concentrations of secondary and tertiary alcohols so that its effect would be constant throughout the series studied. The effect of the side reaction is indicated by the differences in K_{eq} obtained when the concentration of p-Cl and p-methyl tertiary alcohol is changed from 0.15 to 0.20 *M* and 0.05 to 0.07 *M*, respectively (see Table III).

TABLE III

RESULTS OF ESTER-INTERCHANGE EXPERIMENTS ON THE REACTION $(\mathrm{X{-}TO})\mathrm{CrO_2} + p\text{-}\mathrm{Cl{-}SOH} \rightleftarrows p\text{-}\mathrm{Cl{-}SOCrO_2OT{-}X} + \mathrm{X{-}TOH}$ (temperature 29.7 ± 0.05°, solvent benzene)

Substituent	t-Alcohol concn., mole/l.	Concn. of α-(p-chlorophenyl)-ethanol, mole/l.	Init. concn. of Cr^{+6}, mole/l.	Init. $SOCrO_2OT$ concn., mole/l.	$k$obsd. min.$^{-1}$ (based on $t^{1/2}$)	K_{eq} Based on $k_d = 3.6 \times 10^{-2}$	K_{eq} Based on $k_d = 1.8 \times 10^{-2}$
	0.05	0.05			0.0325		
					.0330		
					.0348		
p-NO_2				[a]	.0361		
	.05	.10			.0355		
					.0365		
			0.0145	0.00416	.01019	5.33	22.4
	.30	.025	.0142	.00397	.00993	5.09	20.6
			.00831	.00201	.00861	2.61	8.54
m-Br	.20	.025	.00737	.00166	.00798	2.34	7.26
			.0122	.00420	.0122	3.38	19.0
	.15	.025	.0122	.00400	.0116	3.10	15.8
			.0125	.00280	.00792	2.31	7.46
p-Cl	.20	.025	.01010	.02218	.00767	2.19	6.75
				[b]	.01315		
	.20	.025		[b]	.01255		
			.01100	.00246	.00794	2.31	6.84
	.40	.05	.01125	.00238	.00752	2.14	6.19
p-H	.10	.025	.00986	.00256	.00924	1.30	4.68
			.00924	.00248	.00953	1.37	5.00
	.05	.025	.00748	.00259	.0123	0.890	4.54
			.00748	.00257	.0122	.878	4.41
p-CH_3	.07	.025	.00961	.00218	.00804	.682	2.22
			.00972	.00232	.00847	.732	2.47
p-C_4H_9	.05	.025	.00896	.00976	.00976	.580	2.23
			.00814	.00922	.00922	.552	1.99
t-Butyl alcohol	.0475	.05	.01222	.00911	.00811	.162	0.539
			.01167	.00755	.00755	.151	0.475

[a] 0.3 M nitrobenzene added. [b] Reaction flask in these runs was illuminated by a G.E. reflector sunlamp, 275W, 110–125V, placed 4–5 inches from the flask. Solution temperature was kept the same as for all other runs.

TABLE IV

EXPERIMENTS ON THE EFFECT OF ADDING t-BUTYL ALCOHOL TO VARIOUS REACTION MIXTURES

Secondary alcohol is α-(p-nitrophenyl)-ethanol in each case; conditions, temperature = 29.7 ± 0.05°

	88.2% HOAc, μ 0.20 HCl = 0.172 M	50% HOAc, μ 0.20 H = 0.172 M, Cl^- absent	40% pyridine–60% benzene
k_2 with no t-butyl alc. present	1.63	0.378	0.409
k_2 with t-butyl alc. present	1.35 (0.207 M t-BuOH added)	0.363 (0.207 M t-BuOH added)	0.407 (0.316 M t-BuOH added)

ter, if formed, is low.[13] The expected inhibition by t-butyl alcohol would not be too great, then, even at a concentration of about 0.2 M. However, in 88.2% acetic acid it was evident that 0.207 M t-butyl alcohol inhibited the rate of oxidation of α-(p-nitrophenyl)-ethanol to the extent of about 17%. Another interesting observation was the comparative inhibition of t-butyl alcohol in a medium of only 50% acetic acid. In this case 0.207 M tertiary alcohol did not inhibit the rate within the limits of experimental accuracy. If these observations were due to the competitive esterification reaction by the tertiary alcohol, the relative variation in inhibition by t-butyl alcohol when the solvent was altered from 88.2 to 50% acetic acid affords supporting evidence for the proposal of Westheimer[2e] that the increase in rate of oxidation observed may be due principally to a larger equilibrium concentration of chromate ester in a medium of higher acetic acid content.

Comparison of ρ-Constants.—The ρ-constant for the reaction in benzene (equation A) as obtained from the slope of Fig. 4 was +0.94. For application as ρ (esterification) in equation B the sign of this

$$\begin{array}{c} \mathrm{HCrO_4^-} + \mathrm{ROH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RO{-}CrO_3^-} + \mathrm{H_2O} \\ \downarrow k_d \\ \text{products} \end{array} \qquad \text{(B)}$$

value must be reversed and thus

$$\rho_{\text{obsd}} = \rho_{\text{esterifn}} + \rho_{\text{decompn}} \qquad \text{(C)}$$

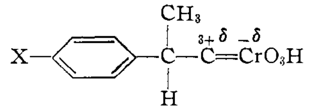
---

[13] Westheimer and Cohen in reference 2e found that the reaction is purely second order up to isopropyl alcohol concentrations of 0.2 M in 86.5% acetic acid solution wherein $k_{\text{obsd}} = k_{(\text{dec})} \times K_{\text{eq}}[i\text{Pr}][\text{Ce}^{+6}]$, and

$$K'_{\text{eq}} = \frac{[\text{chromate ester}]}{([i\text{-Pr}] - [\text{chromate ester}])([\text{Cr}^{+6}] - [\text{chromate ester}])} \cong \frac{[\text{chromate ester}]}{[i\text{Pr}][\text{Cr}^{+6}]}$$

assuming the equilibrium concentration of chromate ester to be very small at isopropyl alcohol concentrations of less than 0.2 M. The falling off of $k_{\text{obsd.}}$ at higher concentrations (0.2–0.5 M) could be attributed to the breakdown of this assumption.

For the reactions studied in pyridine–benzene medium (Table I) it is interesting to observe that solution of equation C for ρ_{dec} gives a value of $0.94 - 0.37 = +0.57$. This quantity can be only a very crude approximation since the solvent is modified by pyridine and the original ρ_{esterifn} was computed for tertiary alcohols in a slightly different reaction. However, the sign of $\rho_{\text{decompn.}}$ as determined here is of an order expected for the elimination (E_2) reaction mechanism discussed above. The magnitude is considerably smaller than observed by Cristol and co-workers[6] for an E_2 mechanism leading to olefin products where, presumably, carbon was required to tolerate considerable negative charge density in the transition state.[14] Here the negative charge on carbon is apparently much smaller. We attribute this to the inductive influence of the oxygen at the seat of reaction. Furthermore, contributing structures such as



$$X-C_6H_4-\underset{H}{\overset{CH_3}{C}}-\overset{3+\delta}{C}=\overset{-\delta}{Cr}O_3H$$

where Cr^{+6} has expanded its octet,[15] enhance the inductive influence of this oxygen atom and thereby increase the apparent capacity of the carbinol carbon for negative charge. The requirement for assistance from a ring substituent for tolerating negative charge in the transition state would therefore be small and would account for a smaller positive ρ-value than is observed in a normal E_2 mechanism leading to olefin products.

It is difficult at this writing to propose a suitable explanation for the ρ_{decompn} noted in the uncatalyzed oxidation reaction in benzene. The observations that seem worthy of emphasis are (a) no decrease in rate when secondary and tertiary alcohol concentrations are doubled (see data for p-Cl-TOH in Table III), and (b) irradiation by an intense source increases the reaction rate by about 65% (similarly noted in reference 2c).

Experimental

Preparation of Secondary and Tertiary Alcohols Used in the Study.—All alcohols used were synthesized by standard techniques, except 2-(p-nitrophenyl)-2-propanol. Their physical constants agreed well with the literature in all cases.

Preparation of 2-(p-Nitrophenyl)-2-propanol.—p-Nitrocumene (92 g.) was added to a solution of 375 ml. of acetic anhydride and 300 ml. of acetic acid. Chromic anhydride (45 g.) was added in small portions over a three-hour period while the solution was stirred and temperature maintained between 23–30°. After the reaction was complete the mixture was poured onto 2 kg. of cracked ice and stirred vigorously while 100 g. of sodium bicarbonate was added portionwise. The solution was allowed to stand overnight and then extracted with two 400-ml. portions of ether. The ether solution was washed carefully with water, again with sodium bicarbonate solution and finally dried over anhydrous potassium carbonate. After removal of solvent at the water-pump the residue was fractionated with a small Vigreux column under high vacuum. p-Nitrocumene (42 g.) was recovered in the forerun. The product fraction (44 g.) consisted mainly of the desired material. This product was treated with alcoholic potassium hydroxide (to remove any traces of acid which might lead to dehydration) and finally redistilled. The yield of pure material used for the kinetic runs was 48%, b.p. 120.5–121° (2 mm.), $n^{19.2}D$ 1.5552. *Anal.* Calcd.: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.8; H, 6.05; N, 7.68.

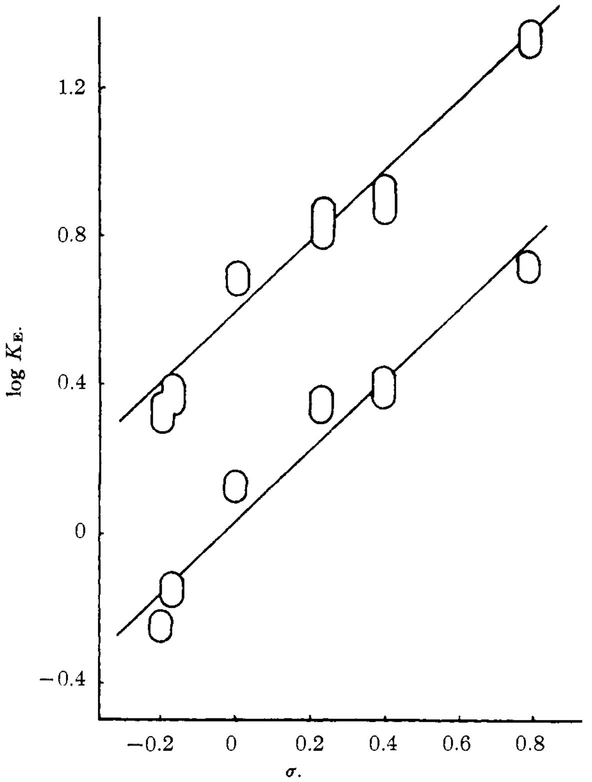


Fig. 4.—Plot of log K_E *vs.* the Hammett σ-constant for the data in Table III (ester interchange equilibria). The lengths of the ovals represent the range of experimental results found. The upper curve is for the results calculated on the basis of $k_d = 1.8 \times 10^{-2}$, the lower curve is based on $k_d = 3.6 \times 10^{-2}$.

Kinetic Runs in Aqueous Acetic Acid.—The alcohol was weighed into a 250-ml. volumetric flask to give a concentration between 0.015 and 0.05 *M*. Acetic acid then was introduced by pipet, the flask made up to volume with water and an aliquot of perchloric acid solution to give the desired hydrogen ion concentration. The flask was immersed in the constant temperature bath for 30–40 minutes. Then 5.00 ml. of a 0.2 *M* chromic acid solution was introduced, the flask rapidly shaken and reimmersed in the bath. At the desired time 25-ml. aliquots were pipetted into an erlenmeyer flask containing 0.4–0.5 g. of iodate-free potassium iodide. Residual chromium was determined by titration with 0.01 *N* sodium thiosulfate. All alcohols studied gave excellent second-order rate curves up to and beyond 70% completion. All reactions were found to be about 70% first-order and 30% second-order with respect to hydrogen ion at 0.25 *M* perchloric acid concentration in 30% acetic acid. This follows the trend shown by Westheimer[2a,e] who has found almost complete second-order hydrogen ion dependence with water as the solvent and complete first-order dependence in 86.5% acetic acid.[16]

Runs in 40% Pyridine–60% Benzene.—A stock solution of 0.05 *M* CrO_3 in 80% pyridine–20% benzene was prepared and was found to be stable for several weeks when stored in a refrigerator. The reaction solution was prepared by mixing equal portions of this solution and a benzene solution of the alcohol under study. Both solutions were warmed previously for 30 minutes in the constant tempera-

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[14] C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2814 (1951).

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

[16] The second-order rate constants reported here are related to the third- and fourth-order equations of Westheimer, *et al.* (reference 3c), in the following way: $k_2 = k_3[H^+] + k_4[H^+]^2$. The disappearance of Cr^{+6} in our studies was found (unpublished results) to observe the following dependence; 70% was removed by the k_3 path and the remaining 30% by the k_4 path.

ture bath. Immediately after mixing, 6–7 ml. of solution was transferred to an insulated centrifuge tube previously warmed to reaction bath temperature. Centrifuging required 1.8 minutes after which a 5.00-ml. aliquot was measured rapidly and transferred to an erlenmeyer flask containing 25 ml. of glacial acetic acid, 5 ml. of concentrated HCl and 0.5 g. of potassium iodide. After standing 1.5–2 minutes 5 ml. of chloroform and 25 ml. of water were added and the amount of free iodine was determined volumetrically. (The benzene layer alone made titration difficult due to the great solubility of iodine in this solvent. The addition of chloroform practically eliminated this problem.) The concentration of residual hexavalent chromium was determined in this manner for several time intervals. The concentration of hexavalent chromium was plotted *vs.* time on semi-log paper and the initial concentration of chromium was determined by extrapolation back to zero time. Second-order rate equations were found to hold at least up to 60% completion (usually further). There appeared to be a gradual falling off of the curves beyond this point.

Runs in Benzene Solutions without Catalysis.—Forty ml. of a benzene solution of the tertiary alcohol under study (concn. 0.100 *M*) was treated with 0.5–0.7 g. of CrO_3 in an erlenmeyer flask. After rapid agitation for several minutes the solution was treated with 5 g. of anhydrous sodium sulfate, decanted into another erlenmeyer flask and the process was repeated. The solution was then transferred to a graduated cylinder which was stoppered and immersed in the reaction bath for about 20 minutes. At this time a 25-ml. aliquot was pipetted into the reaction flask which already contained 15 ml. of a benzene solution of the remainder of the tertiary alcohol to be added to the reaction mixture. After 30 minutes in the bath, 10.00 ml. of a 0.125 *M* solution of α-(*p*-chlorophenyl)-ethanol in benzene were introduced by pipet. The mixture was shaken rapidly and returned to the bath. Three and one-half minutes before a determination was to be made 6–7 ml. of solution were removed to the insulated centrifuge tube and residual chromium was determined in the same manner as in the pyridine–benzene runs. A plot of log (CrO_3) *vs.* time showed a good first-order curve. The half-life of the reaction was determined from the plot obtained and was used to calculate the first-order rate constant. Reproducible rates were obtained only when all glassware was cleaned by a concentrated sulfuric acid wash, several water washes and two rinses with acetone.

The data for condition C in Table I were obtained in a similar manner. The diester of 2-(*p*-nitrophenyl)-2-propanol was prepared as described in the preceding paragraph and added to a 25.00-ml. benzene solution of the secondary alcohol (0.20 *M*) being run. This made the tertiary alcohol concentration 0.25 *M* and the secondary alcohol concentration 0.10 *M*. This solution then was run as described above.

Appendix

Method for Treatment of Data Obtained in Uncatalyzed Benzene Runs.

—Assuming the ester interchange equilibria suggested by Westheimer[3d]

$$\begin{tikzcd}
(\mathrm{TO})_2\mathrm{CrO}_2 + \mathrm{SOH} \arrow[r, shift left, "k_1"] & \mathrm{SOCrO_2OT} + \mathrm{TOH} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_d"] \\
 & \text{Products (P)}
\end{tikzcd}$$

The ester interchange equilibrium thus may be expressed by the equation

$$K_{eq} = k_1/k_{-1} = [\mathrm{SOCrO_2OT}][\mathrm{TOH}]/[(\mathrm{TO})_2\mathrm{CrO_2}][\mathrm{SOH}] = [\mathrm{SOCrO_2OT}][\mathrm{TOH}]/[\mathrm{Cr}^{+6}\text{—}\mathrm{SOCrO_2OT}][\mathrm{SOH}] \quad (1)$$

where Cr^{+6} is the total hexavalent chromium in solution. Solving for the "reactive" component ($SOCrO_2OT$) we have

$$[\mathrm{SOCrO_2OT}] = K_E\left[\frac{\mathrm{SOH}}{\mathrm{TOH}}\right][\mathrm{Cr}^{+6}]\Bigg/1 + K_E\left[\frac{\mathrm{SOH}}{\mathrm{TOH}}\right] \quad (2)$$

Since from the equation for first-order reactions

$$\mathrm{d}P/\mathrm{d}t = k_d[\mathrm{SOCrO_2OT}] \quad (3)$$

Substitution gives

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_d\,K_E{}^{[\mathrm{SOH/TOH}]}\,[\mathrm{Cr}^{+6}]/1 + K_E\,[\mathrm{SOH/TOH}] \quad (4)$$

Solution for K'_E gives the expression

$$K_{eq} = \frac{\mathrm{d}P}{\mathrm{d}t}\left[\frac{\mathrm{TOH}}{\mathrm{SOH}}\right]\Bigg/k_d[\mathrm{Cr}^{+6}] - [\mathrm{d}P/\mathrm{d}t] \quad (5)$$

The equation may be further simplified by noting that

$$\mathrm{d}P/\mathrm{d}t = k_{obsd}[\mathrm{Cr}^{+6}] \quad (6)$$

where k_{obsd} is the actual first-order rate constant for a given run, determined from the half-life time by the equation $k_{obsd} = 0.693/t^{1/2}$. Since one mole of ketone, *P*, is formed for every mole of Cr^{+6} reduced, it follows that the factor $[dP/dt]$ at zero time is the product of the observed first-order decomposition constant, k_{obsd}, and the concentration of Cr^{+6} at zero time. Substituting this factor for dP/dt in equation 5 and simplifying, we obtain

$$K_{eq} = \frac{k_{obsd}\,[\mathrm{TOH/SOH}]}{k_d - k_{obsd}} \quad (7)$$

The factor [TOH/SOH] must be obtained from an analysis of the equilibrium

$$\begin{array}{ccccccc}
(\mathrm{TO})_2\mathrm{CrO}_2 & + & \mathrm{SOH} & \rightleftarrows & \mathrm{SOCrO_2OT} & + & \mathrm{TOH} \quad (8) \\
(\mathrm{Cr}^{+6} - X) & & (A - X) & & (X) & & (B - 2\mathrm{Cr}^{+6} + X)
\end{array}$$

where

A = the amount of secondary alcohol initially introduced into solution
B = the same for the tertiary alcohol
Cr^{+6} = the total hexavalent chromium in solution
X = the concentration of "active" secondary–tertiary chromate. This may be determined by considering equations 3 and 6.

Since the values $k_d[SOCrO_2OT]$ and $k_{obsd}(Cr^{+6})$ are both equal to dP/dt, they are also equal to each other, and

$$k_d\,[\mathrm{SOCrO_2OT}] = k_{obsd}\,[\mathrm{Cr}^{+6}] \quad (9)$$

Acknowledgment.—We are grateful to Mr. T. F. Sanderson of the Experiment Station, Hercules Powder Co., for suggesting the conditions ultimately employed for the synthesis of 2-(*p*-nitrophenyl)-2-propanol described in method 4.

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