In runs made with more than 2 *M* potassium isopropoxide the reaction mixture became dark brown during the addition of the chloroform and yields of acetone and methylene chloride were considerably higher. In one run with 2.2 *M* base, 28% methylene chloride and 4% acetone were found and a considerable amount of black tar remained after the distillation of the orthoester. The formation of this dark color could not be diminished by the addition of diphenylamine to the reaction solutions nor were the yields of the products observed changed significantly by the presence of this inhibitor (0.5 g. per 250 ml.). The dark color could not be brought forth in reactions of 1 *M* potassium isopropoxide by ultraviolet illumination of the reacting solution nor by the addition of small amounts of carbon tetrachloride or methylene chloride.

The Reaction of Potassium Isopropoxide and Bromoform.—By techniques like those described in the reaction of chloroform, 250 ml. of about 1.9 *M* potassium isopropoxide and 16 ml. (0.18 mole) of bromoform gave 48.5 g. (0.41 mole) of potassium bromide, 0.033 mole (18%) of propylene, 0.06 mole (33%) of carbon monoxide, 0.017 mole (9%) of diisopropyl ether, 0.022 mole (12%) of acetone, 0.029 mole (16%) of methylene bromide and 0.006 mole (3%) of triisopropyl orthoformate. Also formed was an even darker reaction solution and residue than observed in the reaction of chloroform. The formation of this color was not diminished nor the yields of the observed products changed significantly by the addition of diphenylamine.

Acknowledgment.—This work was supported in part by the Office of Naval Research to whom the authors wish to express their indebtedness.

ATLANTA, GA.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

The Chromic Acid Oxidation of Pinacol[1]

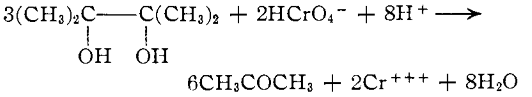
BY Y. W. CHANG AND F. H. WESTHEIMER

RECEIVED JULY 20, 1959

Chromic acid in aqueous solution oxidizes pinacol quantitatively to acetone; the rate is proportional to the concentrations of pinacol, hydrogen ion and the acid chromate ion, $HCrO_4^-$, and reaction proceeds 2.7 times as fast in D_2O as in H_2O. By contrast, pinacol monomethyl ether is oxidized with complex kinetics, and at a rate very small compared to that of pinacol itself. The oxidation of pinacol by chromic acid induces the oxidation of Mn^{++} to MnO_2, with a low "induction factor." These facts can be correlated with a mechanism for the reaction which involves a chromic acid ester of pinacol as an intermediate.

The rate of the chromic acid oxidation of isopropyl alcohol is proportional to the concentration of the alcohol, and of acid chromate ion; the kinetic expression contains two terms, one proportional to the first power, one to the square of the hydrogen ion concentration.[2] The carbon–hydrogen bond at the secondary carbon atom is cleaved during the rate controlling step of the reaction,[3] and the first step of the process probably produces a compound of tetravalent chromium.[4,5] Similar kinetics have been observed for other alcohols,[6] and for aldehydes,[7] and independent evidence for an intermediate of tetravalent chromium (in moderately concentrated sulfuric acid solutions) has been found.[8] Two alternative mechanisms have been suggested for the oxidation process: (a) The reaction may proceed by the decomposition of an ester of chromic acid,[9] or (b) the reaction may proceed by direct attack of the oxidizing agent upon the secondary hydrogen atom of the alcohol.[2,10]

The oxidation of pinacol by chromic acid provides a more clean-cut system for study, since the compound contains no hydrogen atom alpha to the hydroxyl group, and cannot therefore undergo reaction by abstraction of hydrogen from carbon. Recently, Chatterji and Mukherjee[11] have examined the kinetics of the chromic acid oxidation of pinacol.



$$3(CH_3)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(CH_3)_2 + 2HCrO_4^- + 8H^+ \longrightarrow 6CH_3COCH_3 + 2Cr^{+++} + 8H_2O \quad (1)$$

The present research is concerned with this same reaction, and supplements the earlier work. In particular, the rate of the oxidation was found to be 2.7 times as fast in D_2O as in H_2O. This fact has been interpreted to show that the reaction is unlikely to require the cleavage of the O–H bond in pinacol in the rate-controlling step of the process. Furthermore, the rate of oxidation of the monomethyl ether of pinacol is very slow relative to that of pinacol itself. The data are best correlated with an ester mechanism.

Experimental

Materials.—Anhydrous pinacol was prepared by azeotropic distillation of the recrystallized hexahydrate with benzene. The properties of the fraction boiling at 172°, and melting at 43.5–44.2° (corrected) were unchanged by two recrystallizations from benzene–petroleum ether mixtures. Pinacol hexahydrate was recrystallized from water, but the crystals are not stable in air, and lose part of their water of crystallization; solutions of the hydrate were standardized by periodate titration.

Pinacol monomethyl ether was prepared by a modification of the method of Lindner.[12] The potassium salt of pinacol was prepared by refluxing potassium *t*-butoxide with pinacol

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[1] Presented at the Symposium on the Oxidation of Organic Compounds, Queen Mary College, London, April 13–14, 1959.

[2] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); see also ref. 9.

[3] N. Nicolaides and F. H. Westheimer, THIS JOURNAL, **71**, 25 (1949).

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

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

[6] H. G. Kuivila and W. J. Becker, III, THIS JOURNAL, **74**, 5329 (1952); V. Antony and A. C. Chatterji, *Z. anorg. allgem. Chem.*, **280**, 110 (1955); J. Hampton, A. Leo and F. H. Westheimer, THIS JOURNAL, **78**, 306 (1956).

[7] (a) K. B. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958); (b) F. H. Westheimer and G. Graham, *ibid.*, **80**, 3030 (1958).

[8] E. Pungor and J. Trompler, *J. Inorg. Nucl. Chem.*, **5**, 123 (1957).

[9] F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

[10] J. Roček and J. Kurpička, *Chemistry & Industry*, 1668 (1957); *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958).

[11] A. C. Chatterji and S. K. Mukherjee, *Z. physik. Chem.*, **208**, 281 (1958).

[12] J. Lindner, *Monatsh.*, **32**, 403 (1911).

in benzene, and then removing both the benzene and *t*-butyl alcohol by distillation. The finely divided, crystalline potassium pinacolate was refluxed overnight with an excess of redistilled methyl iodide. The resulting mixture was diluted with ether, filtered, washed with water, dried and fractionated to give about a 70% yield of crude pinacol monomethyl ether, b.p. 144–149°. The ether was refractionated in a Precision Distillation Co. concentric tube column, at a reflux ratio of 100/1. The major fraction boiled at 148.5–149°, but nevertheless contained about 5% of impurity as measured either kinetically or by gas–liquid chromatography at 110° over a didodecyl phthalate column in a Perkin–Elmer model 154 Vapor Fractometer. The impurity was not affected by treatment of the crude monoether with acidified periodic acid, but was completely removed by allowing the compound to react, at room temperature, with about 10 mole per cent. of chromic acid in 0.4 *M* perchloric acid solution; after reisolation and distillation, the material boiling at 149° gave a single sharp peak in gas-liquid chromatography and internally consistent kinetics. *Anal.* (S. Nagy) Calcd. for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 63.64; H, 12.29.

Eastman Kodak Co. white label *p*-toluenesulfonic acid was recrystallized from water, and dried in a vacuum desiccator; it titrated correctly for the monohydrate. The corresponding deuterio acid was prepared by dissolving the compound in D_2O and lyophilizing; the procedure was repeated three times. Reagent grade perchloric acid (70% aqueous solution) was standardized before use. Both Merck and Baker acids were used, and one sample was distilled in vacuum prior to standardization. The corresponding deuterio acid was prepared by diluting 30 cc. of 70% aqueous perchloric acid with 30 cc. of D_2O, and removing about 30 cc. of water from the mixture by distillation under vacuum; the process was repeated three times. The D_2O was obtained from the Atomic Energy Commission, and was 99.7% isotopically pure. Sodium *p*-toluenesulfonate, sodium perchlorate and manganous sulfate were recrystallized from water; manganic acetate was prepared according to Brauer.[13] Other chemicals were of reagent grade.

Kinetic Methods.—The rates here reported were determined by spectrophotometry, calorimetry and titration. The spectrophotometric measurements were made with a Beckman model DU spectrophotometer at 3500 Å. in a 1-cm. Corex cell for the solutions containing 0.0006 to 0.0012 *M* chromic acid; more concentrated solutions were measured at the same wave length but with the insertion of quartz "spacers" which cut down the path length for the light to 0.5 mm. A calorimetric method was used for solutions very concentrated in chromic acid. The crude nonadiabatic calorimeter[14] had a thermal leak of 0.0018°/°min. The final point, in calorimetric experiments, could be obtained by the method of Roseveare,[15] so that the errors caused by thermal leak may be minimized. The rates determined by calorimetric and spectrophotometric methods were compared at 25°, and agreed within experimental error; no differences were found in the constants obtained using distilled anhydrous pinacol, recrystallized anhydrous pinacol, recrystallized pinacol hexahydrate or unpurified B.D.H. anhydrous pinacol; the rates with Merck, Baker and distilled perchloric acids were the same within 5%. The rate constant determined by titration are discussed later (see section on Results).

Most of the rates were determined under experimental conditions where all the concentrations were sensibly unchanged, during any experiment, except for that of the chromic acid; the rate was first order in $HCrO_4^-$. Where the concentration of chromic acid was higher than 0.003 *M*, the method of graphical integration[2] was used to obtain rate constants.

Induction factors were determined by the technique of Watanabe and Westheimer.[4]

Products.—The acetone from the oxidation of pinacol was isolated by the method used previously.[2] The yield of crude 2,4-dinitrophenylhydrazone was 93% or greater based on the stoichiometry of equation 1; correction for loss during the analytical procedure brings the corrected yield above 96%. The crude product melted at 122–124°; the recrystallized compound melted at 124–125°, and did not depress the melting point of an authentic sample of acetone 2,4-dinitrophenylhydrazone; on the other hand, the melting point of a mixture with the 2,4-dinitrophenylhydrazone of pinacolone (m.p. 124°) was 106–111°. This yield of product is considerably greater than the 67% reported by Chatterji and Mukherjee.[11] The discrepancy is caused in part by the fact that the Indian scientists used slightly less acid than is required by the stoichiometry of eq. 1. However, even under their conditions, the yield of 2,4-dinitrophenylhydrazone we obtained exceeds that which they reported.

Reaction of Pinacol with Mn^{+++} and with MnO_2.—A freshly prepared solution of 0.36 g. of manganic acetate in 20 cc. of 4 *N* perchloric acid was mixed quickly with a solution of 0.100 g. of pinacol hexahydrate in 4 cc. of water. The solution was initially cloudy and MnO_2 started to precipitate, but after 10 minutes the solution cleared. A 90% yield of acetone was isolated (as the 2,4-dinitrophenylhydrazone) from the clear solution.

In another experiment, 0.05 g. of manganic acetate was mixed with 5 cc. of 4 *N* $HClO_4$, and allowed to stand a few minutes to precipitate MnO_2. Pinacol hydrate (15 mg.) was added to this suspension and, after 6 minutes of shaking, all the precipitate went into solution.

Oxygen Effect.—The rate of the chromic acid oxidation of pinacol carried out in vacuum was about 10% less than that of a sample into which oxygen was bubbled. Since the difference is small, no precautions to remove oxygen usually were taken.

Results

The third-order rate constants for the oxidation of pinacol by $HCrO_4^-$ in aqueous solutions of *p*-toluenesulfonic acid at 30° and an ionic strength of 0.40 are collected in Table I; similar data for perchloric acid solutions are presented in Table II.

TABLE I

RATES OF OXIDATION OF PINACOL AT 30°
(*p*-TOLUENESULFONIC ACID)

Pinacol, *M*	Chromic acid, *M*	*p*-Toluenesulfonic acid, *M*	*k*, (l./m.)^2 min.$^{-1}$
0.010	0.00060	0.025	42
.020	.00060	.025	42
.040	.00060	.025	43
.080	.00060	.025	44
.18	.00060	.025	43
.010	.00060	.050	42
.010	.00060	.100	42
.010	.00060	.20	42
.010	.00060	.40	41
.010	.00032	.025	42
.010	.0012	.025	41
.010	.0034	.025	45
.010	.010	.025	45
.010	.00060	.100	35 (vac.)
.010	.00060	.100	37 (vac)
.010	.00060	.100	38 (vac.)

The first-order rate constants, calculated on the basis of the total hexavalent chromium present in the solution, decreased with increasing concentration of chromic acid. However, the data in column 4 of Table I were computed on the assumption that the only oxidizing species is the acid chromate ion, and that the equilibrium constant[2,16] at an ionic strength of 0.4 for the hydration of dichromate is

$$(\mathrm{HCrO_4^-})^2/(\mathrm{Cr_2O_7^=}) = 0.015 \text{ mole/liter} \qquad (2)$$

The data of Chatterji and Mukherjee[11] show a de-

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[13] G. Brauer, "Handbuch der präparativen anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954.

[14] F. H. Westheimer and M. S. Kharasch, THIS JOURNAL, **68**, 1871 (1946); L. Larsson and P. Bergner, *Arkiv Kemi*, **13**, 143 (1958).

[15] W. E. Roseveare, THIS JOURNAL, **53**, 1651 (1931).

[16] J. Tong and E. King, *ibid.*, **75**, 6180 (1953).

TABLE II

RATES OF OXIDATION OF PINACOL (PERCHLORIC ACID); IONIC STRENGTH, 0.40

Pinacol, *M*	Chromic acid, *M*	$HClO_4$, *M*	*T*, °C.	k_3, l.²/m.² min. Spectrophotometric	Titrimetric
0.010	0.0006	0.10	30	37	
.010	.0010^a	.10	30	33	
.017	.0005^a	.10	30	39	
.017	.0005^a	.10	30	38	
.010	.0005^a	.10	30	39	
.010	.0006	.20	30	35	
.010	.0006	.20	30	33 (vac.)	
.010	.0006	.20	30	33 (vac.)	
.010	.0006	.10	35	59^b	
.010	.0006	.20	35	58^b	
.010	.0006	.20	35	54 (vac.)	
.010	.0006	.10	35	55 (vac.)	
.020	.0015	.20	35	60^{b,c}	
.010	.0006	.10	35		44 (air)^b
.010	.0006	.10	35		50 (N_2)^b
.010	.0006	.10	35		55 (N_2, ampoules)^b

^{a} Introduced as potassium dichromate. ^{b} Average of two concordant experiments. ^{c} Calorimetric.

crease in rate constant with increasing chromic acid concentration which can also be accounted for at least approximately on the assumption that the acid chromate ion and not the dichromate ion is the oxidant.

Our data, like those of Chatterji and Mukherjee, show that the reaction is first order in pinacol and first order in hydrogen ion; both sets of data, properly interpreted, show that the rate is first order in acid chromate ion. However, the absolute magnitudes of the rate constants differ somewhat. The data in Tables I and II show that the rate is somewhat faster with *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate than with perchloric acid and sodium perchlorate; such specific salt effects at an ionic strength of 0.4 are not uncommon. But the rate constants, determined spectrophotometrically or calorimetrically in the presence of $HClO_4$ at 35° and reported in Table II exceed the constant of 42 l.²/m.²min., reported by the Indian workers, by about 30-35%. Although the discrepancy is not large, considerable effort has been expended in determining its cause. As reported in the Experimental section, rates were measured with pinacol purified in four different ways, with perchloric acid from three sources, with both recrystallized chromic acid and with potassium dichromate as oxidant, with two different samples of recrystallized sodium perchlorate, and with deionized and redistilled water. Chloride ion is known to inhibit chromic acid oxidations,[17] but its effect in the present case is small, and traces of chloride in the perchlorate cannot be responsible for the rate differences. However, as shown in Table II, the data of Chatterji and Mukherjee are reproducible; the rate constant, determined titrimetrically in air, agrees closely with that they report. By contrast, when the reaction was conducted under nitrogen (and followed by titration), the rate constant was considerably higher; and when the reaction mixture was divided into individual nitrogen-filled ampoules, the rate determined by titration rose to a value close to that observed spectrophotometrically. Furthermore, when the reaction was followed spectrophotometrically in evacuated cells, the rate fell a few per cent. Presumably the rates determined by titration in air are considerably too low, those determined spectrophotometrically somewhat high; the correct rate constant is probably about 10% lower than that reported for the spectrophotometric runs in air.[18] These differences stand out in contrast to those for isopropyl alcohol, where titration[2,4] and spectrophotometry[3] give identical results. However, Wiberg and his collaborators[19] have found that the rates of the chromic acid oxidation of diphenylmethane and of benzaldehyde are 40-50% less in the presence of air than they are when the reactions are conducted under nitrogen; the rates in both cases were determined titrimetrically. The influence of air on chromic acid oxidations had been noted much earlier by Waters.[20] Although, in the present instance, the detailed significance of the effect of air has not been elucidated (and constitutes an interesting point of departure for future studies), nevertheless the data show that, in the presence of air, the results obtained titrimetrically are systematically lower than those observed spectrophotometrically. Probably the best rate constants are those reported in Tables I and II for experiments conducted in vacuum.

Isotope Effect.—The rates in H_2O and D_2O are presented in Table III.

TABLE III

RATE CONSTANT FOR THE CHROMIC ACID OXIDATION OF PINACOL AT 30° IN AIR

Initial concentrations: pinacol, 0.010 *M*; *p*-toluenesulfonic acid, 0.050 *M*; chromic acid, 0.0006 *M*

Ionic strength	*k*, (l./m.)² min.⁻¹ H_2O	D_2O	$k(D_2O)/k(H_2O)$
0.40	42.5	113.4	2.67
.05	43.8	121.5	2.77
.05	43.4	121.6	2.80

Induction Factor.—Pinacol "induces" the oxidation of Mn^{++} to MnO_2 by chromic acid. The induction factor has been calculated from the moles of MnO_2 precipitated divided by the moles of pinacol consumed. The data for various concentrations of chromic acid, manganous ion, pinacol and *p*-toluenesulfonic acid are shown in Fig. 1. Each curve refers to the variation of the concentration of one reactant; each set of experiments was conducted with constant concentrations of three reagents near those which maximize the induction factor. The time chosen for isolation of the MnO_2 was roughly three half-lives. Inspection of the figure shows that the maximum induction factor observed was slightly less than 0.3.

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[17] M. Bobtelsky and Ch. Radovensky-Cholatnilow, *Z. anorg. allgem. Chem.*, **199**, 241 (1931); M. Cohen and F. H. Westheimer, THIS JOURNAL, **74**, 4387 (1952).

[18] The authors are indebted to Dr. William Giddings and Professor Kenneth B. Wiberg of the University of Washington who carried out a single experiment at 30°; their constant of 32 l.²/m.² min. is somewhat lower than the average value of 37 we obtained in air, and close to the value of 33 we obtained in vacuum.

[19] K. B. Wiberg, private communication.

[20] W. A. Waters, *Trans. Faraday Soc.*, **42**, 184 (1946); A. Robertson and W. A. Waters, *ibid.*, **42**, 201 (1946); W. A. Waters, *J. Chem. Soc.*, 1151 (1946).

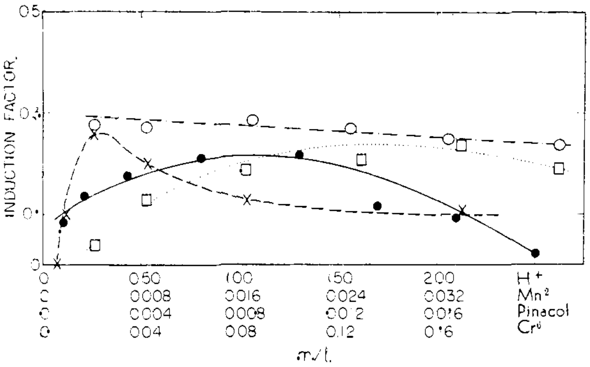


Fig. 1.—The induction factor in the oxidation of pinacol by chromic acid as a function of the concentrations of acid, manganous ion, pinacol and chromic acid: (H^+), ● ———; (Mn^2), O – · – · –; (pinacol), X – – – –; (Cr^{6+}), □ . . . . . .

Rates in the Presence of Mn^{++}.—At low concentrations of chromic acid, no MnO_2 precipitates, and the rate of the oxidation is diminished to one third of that in the absence of manganous ion. This is the result which will be expected if manganous ion catalyzes the disproportionation of the intermediate valence states of chromium, and the rate will be diminished by the same factor regardless of whether the first product is tetravalent chromium or pentavalent chromium. At higher concentrations of chromic acid, the rates (determined calorimetrically) showed no effect of manganous ion, even though, under these circumstances, some MnO_2 was precipitated. The data are presented in Table IV.

TABLE IV

EFFECT OF Mn^{++} ON RATE AT 30° AND IONIC STRENGTH OF 0.40 AND 0.70 IN AIR

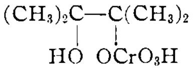
Pinacol	T, °C.	μ	Chromic acid	$HClO_4$	Mn^{++}	k, (l./m.)^2 min.$^{-1}$
0.010	30	0.40	0.00060	0.097	0.000	38.8
.010	30	.40	.00060	.097	.007	37.7
.010	30	.40	.00060	.097	.014	35.3
.010	30	.40	.00060	.097	.070	21.3
.010	30	.70	.00060	.097	.14	15.8
.0050	25	.70	.145	.194	.000	23.2^a
.0050	25	.70	.145	.194	.0193	23.1^a
.010	25	.70	.145	.425	.000	23.1^a
.010	25	.70	.145	.425	.0193	23.1^a
.0050	25	.70	.145	.425	.000	23.2^a
.0050	25	.70	.145	.425	.0193	23.3^a

^{a} Determined by calorimetry.

Pinacol Monomethyl Ether.—The rate constants for individual experiments were essentially zero order with respect to chromic acid, but the apparent zero-order constants are not uniform over the concentration range from 0.0003 to 0.003 M. When the chromic acid concentration is 0.00060 M, that of p-toluenesulfonic acid, 0.40 M, and the concentration of the ether 0.10 M, the approximate zero-order rate constant for the disappearance of chromic acid is 4.8 × 10^{-7} m./l. min. at 30°. Although comparison of two rates of different orders cannot strictly be made, the rate of the chromic acid oxidation of pinacol, at comparable concentrations to those above, is about 1,500 times as fast as that of the ether. The products in the latter case contain acetone, but the yield is poor.

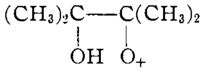
Discussion

The data in this paper can be interpreted on the assumption that the first step in the chromic acid oxidation of pinacol is the formation of an ester



$$\begin{array}{cc}(CH_3)_2C & —C(CH_3)_2 \\ | & | \\ HO & OCrO_3H\end{array}$$

The fact that pinacol is oxidized very much more rapidly than is pinacol monomethyl ether suggests that the next step is the formation of a cyclic ester, which then undergoes cleavage. An alternative first step for the oxidation would require the oxidation of pinacol by chromic acid to form the cation



$$\begin{array}{cc}(CH_3)_2C & —C(CH_3)_2 \\ | & | \\ OH & O_+\end{array}$$

a slight modification of this mechanism would postulate that the oxidation by chromic acid at the OH group is accompanied by cleavage of the pinacol to acetone and $(CH_3)_2C{=}OH^+$. However, both of these processes (and any other which requires breaking the OH bond as part of the rate-controlling step) are made improbable by the solvent isotope effect. The reaction proceeds 2.7 times as fast in D_2O as in H_2O. This rate effect is about as large as can be anticipated for a reaction in which $HCrO_4^-$ is protonated to H_2CrO_4 prior to reaction. In general, acids are about 2.5–3.0 times as strong[21] in H_2O as D_2O, and therefore, at a given concentration of p-toluenesulfonic acid, about 2.5 times as much D_2CrO_4 would be present in D_2O as H_2CrO_4 in H_2O. A reaction which proceeds by prior protonation of a substrate should occur about 2.5 times as fast in D_2O as in H_2O, always provided that no O–H bond is broken in the rate-controlling step of the process. Of course, if an O–H bond is broken, then the rate of this latter process will be considerably greater in H_2O than in D_2O. The kinetic isotope effect would compensate, partially or completely, for the isotope effect in the prior equilibrium; under these circumstances, the over-all rate will not be accelerated by a factor as large as 2.5. Pertinent examples have been recorded in the literature.[22] In the present instance, the effect of changing the solvent is so large as effectively to preclude the possibility of breaking an O–H bond in the rate-controlling process. Such being the fact, an ester mechanism for the oxidation of pinacol becomes very probable.

Although the reaction probably proceeds by way of an ester, the data at present available do not permit a decision as to whether the reaction proceeds from the ester to two moles of acetone and an unstable compound of tetravalent chromium, or whether the initial products are acetone, a free radical, and a derivative of pentavalent chromium. The induction factor is low, and this by analogy with the work on the chromic acid oxidation of isopropyl alcohol,[4] suggests that the reaction proceeds to give tetravalent chromium. However, the rapid

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[21] G. Schwartzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

[22] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

reaction of both Mn^{++} and of MnO_2 with pinacol precludes an accurate determination of the induction factor, and the question of the oxidation states of chromium in the reaction pathway had best be left for further investigation.

Acknowledgment.—The authors wish to express their appreciation to the Petroleum Research Fund and the Eugene Higgins Trust for support of this investigation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

Cyclopropanes. V.[1] The Cyclopropylcarbinyl Rearrangement[2]

BY H. M. WALBORSKY AND J. F. PENDLETON[3]

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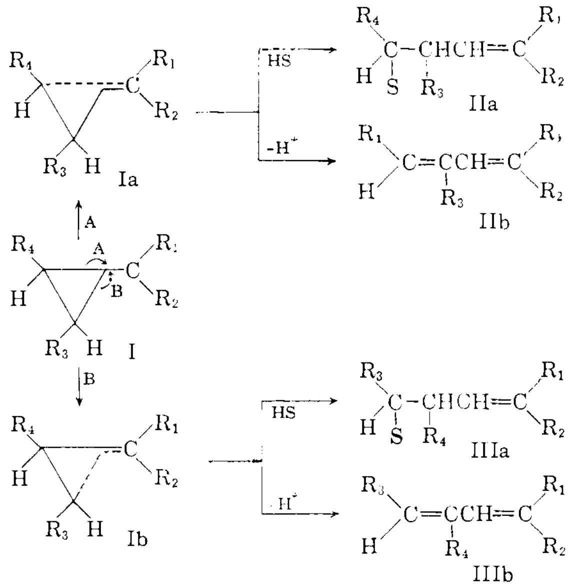
The direction of cyclopropane ring opening is studied by the dehydration of a series of ring-substituted cyclopropylcarbinols. Dehydration of I (R_4 = C_6H_5, $C_6H_5CH{=}CH$ and $C_6H_5CH{=}CHCH{=}CH$; R_3 = H; R_2 = R_1 = C_6H_5 or H) affords IIb. That carbethoxymethylene adds in a terminal fashion was demonstrated by its addition to the terminal double bond of 1-phenylhexatriene. This terminal addition permitted the extension of unsaturation and thus styrene was converted to 1-phenylbutadiene; 1-phenylbutadiene to 1-phenylhexatriene; and finally 1-phenylhexatriene to 1-phenyloctatetraene. The assignment of an all-*trans* configuration to the hydrocarbons IIb by means of their ultraviolet absorption spectra is discussed.

There are numerous examples of cyclopropane ring opening caused by the generation of a positive charge on a carbon adjacent to a cyclopropane ring; *viz.*, a cyclopropylcarbinyl cation I. However, in unsubstituted cyclopropylcarbinyl systems,[4-8] and carbinyl carbon substituted cyclopropylcarbinyl systems[9-14] ring opening can lead to only one product since the two bonds in the ring which can open are equivalent. Ring-substituted cyclopropylcarbinyl cations I on the other hand can give rise to two possible products on ring opening. The cyclopropane ring in I can open at A or B leading to the possible transition states or intermediates Ia or Ib, respectively. Ring opening should occur in such a manner that *that bond will break which leaves the positive charge on the carbon atom which can best delocalize this charge.* Thus, the products obtained will depend on the relative positive charge-delocalizing ability of R_3 and R_4. If R_4 is more capable of delocalizing a positive charge than R_3, then the intermediate Ia will be of lower energy, and preponderance of products arising from this intermediate should be observed (IIa and IIb). Attack of solvent or acid (HS) gives IIa, while direct loss of a proton yields IIb. Support for this hypothesis can be found in the rearrangements observed when the following carbinols are subjected to acid treatment: 2-phenyl-3-carboxycyclopropylcarbinol,[15] α-thujene,[16a] sabinene,[16b] sabinaglycerol[16c] and 2,2-diphenylcyclopropylcarbinol.[17]



The system first studied was the phenylcyclopropyl system. A mixture of *cis*- and *trans*-ethyl 2-phenylcyclopropylcarboxylate(V) had been prepared in good yield by Burger and Yost by the addition of ethyl diazoacetate to styrene.[18] Treatment of this mixture (V) with phenylmagnesium bromide afforded *cis*- and *trans*-(2-phenylcyclopropyl)-diphenylcarbinol (VIa, 20%) and (VIb, 46%), respectively. The assignment of configuration was based on the infrared adsorption data appearing in Table I. The absence of intermolecular hydrogen bonding of VIa and the observed strong intramo-

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[1] For paper IV of this series, see H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1958).

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