

method from 2,3-dimethylbutanoic acid (K & K Laboratories Inc.) in a yield of 61%: bp 136–138° [lit.<sup>34</sup> bp 135.9–136.6° (751 mm)]; ir (neat) 1795 cm<sup>-1</sup> (–COCl).

**2-Ethyl-3-methylbutanoic Acid.** To 450 ml of water in a 1-l. flask fitted with a mechanical stirrer and cooled in an ice bath was added 58 ml (107 g) of concentrated sulfuric acid. When the temperature had fallen to 15°, 72 g (0.50 mol) of 2-ethyl-3-methylbutyraldehyde (Eastman Kodak Co.) was added, followed by 57 g (0.36 mol) of potassium permanganate in 2.5-g portions. The permanganate was added at such a rate that the temperature of the solution did not rise above 20°. When the addition was completed, sodium bisulfite was added until the solution became clear. The oil layer was separated, washed with water, and distilled from a Claisen flask. The foreruns were separated from any water and redistilled. The combined fractions were redistilled at atmospheric pressure to afford 55 g (85%) of product, bp 140°.

**2-Ethyl-3-methylbutanoyl Chloride (16).** To 54.5 g (0.500 mol) of thionyl chloride was added 55 g (0.42 mol) of 2-ethyl-3-methylbutanoic acid at 50° over the course of 1 hr. When the addition was completed, the solution was heated on a water bath for 30 min. Distillation of the solution afforded a crude acid chloride, bp 110–156°, which was purified by redistillation, bp 150–152°, to yield 40 g (64%) of product; ir (neat) 1795 cm<sup>-1</sup> (COCl).

**Stoichiometric Decarbonylation of Hexanoyl Chloride with Chlorotris(triphenylphosphine)rhodium(I).** To a solution of 0.210 g (1.50 mmol) of hexanoyl chloride (Matheson Coleman and Bell) in 10 ml of xylene was added 1.3 g (1.5 mmol) of chlorotris(triphenylphosphine)rhodium(I). The solution was heated to the reflux temperature for 2.5 hr and the olefins were collected in a trap at –78°. Glc analysis (20 ft × 0.375 in. 20% SE-30 Chromosorb W column) indicated the presence of 1-pentene (5.5%) and 2-pentene (94.5%) by comparison with authentic samples.

(34) M. Hommelen, *Bull. Soc. Chim. Belg.*, **42**, 245 (1933).

**Stoichiometric Decarbonylation of Hexanoyl Chloride with Chlorotris(triphenylphosphine)rhodium(I) in the Presence of Triphenylphosphine.** The reaction was carried out as above except with the presence of 1 molar excess of triphenylphosphine. Glc analysis showed no change in the product ratio.

**Catalytic Decarbonylation of Acid Chlorides with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I).** A. **General Procedure for the Decarbonylation of Hexanoyl Chloride.** To a solution of hexanoyl chloride (Matheson Coleman and Bell) in 10 ml of benzonitrile was added 100 mg (0.27 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) and an appropriate amount of triphenylphosphine (Table I). The solution was heated to 190° for a period of 4–24 hr, and the product olefins were collected in a cold trap at –78°. The isomer distribution was analyzed by glc using a 20 ft × 0.375 in. 20% SE-30–Chromosorb W column.

B. **Decarbonylation of the Branched Acid Chlorides.** A typical decarbonylation was carried out as follows. A solution of 570 mg (3.83 mmol) of 2-ethyl-3-methylbutanoyl chloride, 190 mg (1.36 mmol) of triphenylphosphine, and 50 mg (0.14 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) in 10 ml of benzonitrile was heated to 190° for 24 hr. The products were collected by distillation and absorbed in a pyridine–sodium hydroxide solution. Gas chromatography (20 ft × 0.375 in. 20% SE-30–Chromosorb W column) and mass spectral analysis showed: *cis*- and *trans*-4-methyl-2-pentene (46%), *m/e* 84 (M<sup>+</sup>); 2-methyl-1-pentene (10%), *m/e* 84 (M<sup>+</sup>); and 2-methyl-2-pentene (44%) *m/e* 84 (M<sup>+</sup>); yield, 80%.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. M. R. was supported by a National Science Foundation Traineeship during part of his graduate study.

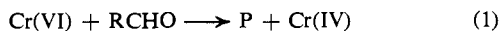
## Chromium(IV) Oxidation of Aliphatic Aldehydes

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**Abstract:** The oxidation of aliphatic aldehydes in aqueous solution by chromium(IV) generated *in situ* from chromium(VI) and vanadium(IV) has been studied. Propionaldehyde is oxidized in a practically quantitative yield to propionic acid. Pivaldehyde gives a mixture of pivalic acid, *tert*-butyl alcohol, and isobutylene. The aldehydes seem to react in their hydrated forms; the value of the  $\rho$  constant for the oxidation of aldehyde hydrates is –0.96. The reaction exhibits a moderate deuterium isotope effect ( $k_H/k_D = 1.7$  for propionaldehyde and  $k_H/k_D = 2.1$  for pivaldehyde), which is consistent with a hydrogen atom transfer in the rate-limiting step from the aldehydic carbon atom to the oxidant. A mechanism for the chromium(IV) oxidation analogous to that earlier suggested for the oxidation of alcohols is proposed, and conclusions concerning the overall mechanism of the chromic acid oxidation of aldehydes are presented.

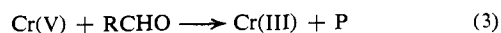
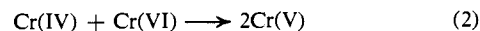
The first step in the chromic acid oxidation of aldehydes is generally thought of as involving a two-equivalent change to give the organic product and chromium(IV). This contention is supported by the



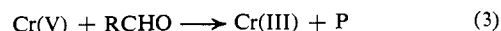
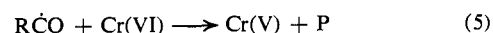
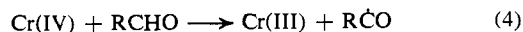
work of Chatterji and Mukherjee,<sup>1</sup> which showed an induction factor of 0.5 in the formaldehyde induced oxidation of manganese(II). However, the fate of chromium(IV) after the initial step has been open to question. Two most frequently cited routes for the fate of chromium(IV) are shown in Scheme I and

(1) A. K. Chatterji and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **80**, 3600 (1958).

### Scheme I



### Scheme II



Scheme II. For a long time, these two schemes were also considered to be possible mechanisms in the oxidation of alcohols. However, recent studies in our laboratory have clearly shown the activity of chromium-

(IV) as an oxidant toward alcohols, and cast doubt on the possibility of Scheme I.<sup>2-4</sup> The activity of chromium(IV) as an oxidant toward alcohols was also supported by the work of Trahanovsky.<sup>5</sup> The validity of Scheme II in the oxidation of isopropyl alcohol was confirmed by Wiberg's experiment on the yield of acetone relative to the amount of chromium(V) generated.<sup>6</sup> Thus, in the alcohol oxidation, the behavior of chromium(IV) has been well established. On the other hand, the available data in the literature at present do not afford a clear-cut choice between the two schemes in the oxidation of aldehydes, nor do they provide any information about the nature of the reaction between chromium(IV) and aldehydes. Using the technique employed in the study of the alcohol oxidation<sup>3</sup> in which both chromium(IV) and chromium(V) are generated *in situ* from chromium(VI) and vanadium(IV), this work examines the behavior of tetravalent chromium toward aliphatic aldehydes.

### Experimental Section

**Materials.** Acetaldehyde (Eastman Chemicals), butyraldehyde (Eastman Chemicals), propionaldehyde (Matheson Coleman and Bell), and chloroacetaldehyde (K & K Laboratory) were purified by fractional distillation through a 14-cm silvered vacuum-jacketed column packed with Nichrome Heli-pak. Formaldehyde was prepared by heating paraformaldehyde (Eastman Chemicals) in a round-bottomed flask by immersing the flask in an oil bath at 180–200°. The formaldehyde gas was introduced into water in an erlenmeyer flask. Dichloroacetaldehyde (City Chemicals) and pivaldehyde (K & K Laboratory) were purified by preparative gas-liquid chromatography using an 80 in. × 0.75 in. silicone rubber SE-30 stainless steel column. Trichloroacetaldehyde (Eastman Chemicals) was distilled through a 14-cm silvered vacuum-jacketed column packed with Nichrome Heli-pak under nitrogen atmosphere and in the dark.

1-Deuteriopivaldehyde and 1-deuteriopropionaldehyde were prepared by controlled chromic acid oxidation of 1,1-dideuterio-n-pentyl alcohol and 1,1-dideuterio-1-propanol, respectively.<sup>8</sup> The deuterated alcohols were in turn prepared by lithium aluminum deuteride reduction of ethyl pivalate and pentyl propionate.<sup>9</sup> The ir spectrum of 1-deuteriopivaldehyde showed absorptions at 2040 and 2130  $\text{cm}^{-1}$  and that of 1-deuteriopropionaldehyde at 2060 and 2090  $\text{cm}^{-1}$ , indicative of the C–D stretching of the CDO group. The nmr spectra of both aldehydes showed no absorption in the aldehydic proton region ( $\delta$  8–12 ppm). The deuterium contents in the aldehyde were determined to be greater than 99% using an Atlas CH-5 mass spectrometer.

All the liquid aldehydes were checked for purity on a F & M 5750 Research Chromatograph before being dissolved in water for oxidation studies. Because of the high volatility of some of these aldehydes, the concentration of the aqueous solutions was determined analytically; the hydroxylamine hydrochloride method<sup>10a</sup> was used for formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde and the dinitrophenylhydrazine method for chloroacetaldehyde and dichloroacetaldehyde.<sup>10b</sup>

Vanadyl sulfate and vanadium pentoxide were Fisher reagents; lithium and barium perchlorate were from C. F. Smith Co.; per-

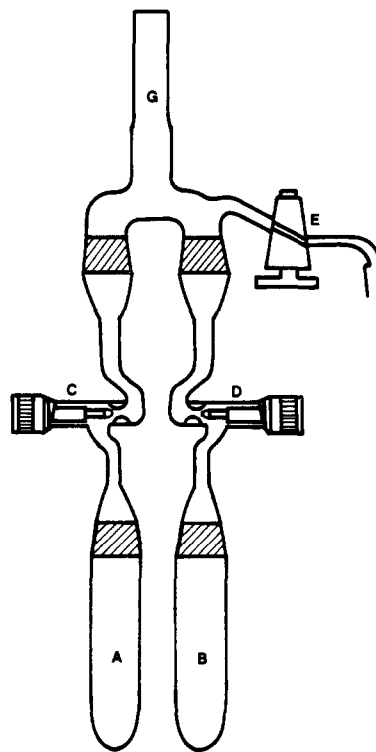


Figure 1. Apparatus for the relative rate determination of the chromium(IV) oxidation of aliphatic aldehydes.

chloric acid was 72% reagent from Baker and Adamson. A. R. grade potassium dichromate (Baker) was used without further purification.

Vanadium(IV) perchlorate solution was prepared by reacting vanadyl sulfate and barium perchlorate using the method of Espenson.<sup>11</sup> A solution of vanadium(V) perchlorate was prepared by stirring vanadium pentoxide in perchloric acid overnight. The concentrations of vanadium(IV), vanadium(V), and chromium(VI) solutions were determined spectrophotometrically.<sup>11</sup>

**Yield of Vanadium(V).** While aqueous solutions of vanadium(IV) alone or in the presence of alcohols are reasonably stable, they become extremely susceptible to air oxidation in the presence of aldehydes. It was therefore necessary to modify extensively the experimental techniques used previously in the study of the chromium(IV) oxidation of alcohols<sup>3</sup> and carry out all measurements in a strictly air-free system.

The yield of vanadium(V) in the reaction was measured by the loss of vanadium(IV) determined spectrophotometrically at 764 nm. The apparatus used in the reaction is shown in Figure 1. Bulb A contained a solution of vanadium(V) and chromium(VI) and bulb B vanadium(IV) and the aldehyde. The system was evacuated for about 15 min at liquid nitrogen temperature and allowed to thaw at room temperature. This process of degassing was repeated four times. The initial concentration of vanadium(IV) was determined spectrophotometrically at 764 nm, after bringing the contents in bulb B into the Pyrex cell G through valve D. Subsequently, the contents of both bulbs were mixed, and the final vanadium(IV) concentration was established. It was found that in order to obtain reproducible results for volatile aldehydes, the solution containing vanadium(IV) and the aldehyde had to be added to the solution of chromic acid in bulb A. When the reverse mixing procedure was used, premature reduction of chromic acid by the aldehyde took place and distorted the results. The time required to reach constant absorbance was about 3 min.

For example, in the study of the oxidation of acetaldehyde, the following amounts of reagents were used in a typical run: 1 ml of 0.0876 M vanadium(V) (0.32 M in  $\text{HClO}_4$ ) plus 0.4 ml of 0.1 M chromium(VI) in bulb A, and 1 ml of 0.195 M vanadium(IV) (0.23 M in  $\text{HClO}_4$ ) and 1 ml of 0.125 M  $\text{CH}_3\text{CHO}$  plus 1.6 ml of  $\text{H}_2\text{O}$  in bulb B. A set of absorbance values at 764 nm was obtained in which the concentration of the acetaldehyde in the mixture was

(2) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); **95**, 7123 (1973).

(3) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

(4) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5462 (1971).

(5) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 1120 (1970); **93**, 4536 (1971).

(6) K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **93**, 2543 (1971).

(7) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 397.

(8) C. D. Hurd and R. N. Meinert, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 541.

(9) R. B. Moffett, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1973, p 834.

(10) S. Siggia, "Quantitative Organic Analysis via Functional Groups," 2nd ed, Wiley, New York, N. Y., 1963: (a) p 74; (b) p 96.

(11) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964).

varied. In a typical set of data, the amount and concentration of the acetaldehyde solution used were: 0; 2.6 ml, 0.125 *M*; 1.0 ml, 0.625 *M*; 2.6 ml, 0.625 *M*; 1.0 ml, 3.125 *M*. The amount of water in bulb B was varied with the amount of aldehyde solution in order to maintain a total volume of 3.6 ml in bulb B.

The aldehydes studied in this manner were: formaldehyde, acetaldehyde, propionaldehyde, 1-deuteriopropionaldehyde, chloroacetaldehyde, dichloroacetaldehyde, trichloroacetaldehyde, pivaldehyde, and 1-deuteriopivaldehyde.

**Kinetic Measurements of the Chromium(VI)-Vanadium(IV) System.** (a) **In the Absence of Acetaldehyde.** An aqueous solution containing vanadium(V) ( $7.15 \times 10^{-6}$  *M*), vanadium(IV) ( $5.46 \times 10^{-4}$  *M*), and LiClO<sub>4</sub> (0.5*M*) in 0.01 *M* HClO<sub>4</sub> was prepared and deaerated. A measured amount of this solution (27 ml) was introduced with a gas-tight syringe into a 10-cm silica cell which had been stoppered with a rubber septum and flushed with nitrogen. After thermal equilibration at 25° for about 30 min, a solution of chromium(VI) (0.934 g, 0.001 *M*) was added with a gas-tight syringe and the absorbance at 350 nm followed with time.

(b) **In the Presence of Acetaldehyde.** An aqueous solution of vanadium(V) ( $6.84 \times 10^{-5}$  *M*), vanadium(IV) ( $6.00 \times 10^{-4}$  *M*), and LiClO<sub>4</sub> (0.5 *M*) in 0.01 *M* HClO<sub>4</sub> was prepared (solution A) and the absorbance at 350 nm determined. A second solution (solution B) contained exactly the same concentrations of the inorganic reagents as solution A, in addition to  $2.64 \times 10^{-2}$  *M* of acetaldehyde. Solution B (27 ml) was pipetted into a 10-cm silica cell, and the absorbance at 350 nm was measured until it reached a constant value. (The increase in absorbance was due to the acetaldehyde-catalyzed air oxidation of vanadium(IV) to vanadium(V)). A weighed quantity of 0.001 *M* chromium(VI) solution (0.959 g) was introduced into the cell and mixed. The absorbance was then followed as a function of time.

The absorbance of solution A (0.097) gave the concentration of vanadium(V) before the air oxidation. The absorbance of solution B (0.271) gave the concentration of vanadium(V) in the solution after the air oxidation of vanadium(IV) and represents the vanadium(V) concentration in the system right before the chromic acid oxidation. The amount of vanadium(IV) being air oxidized to vanadium(V) could be found from the difference between the absorbances of solution B and solution A, and was taken into account in calculating the concentration of vanadium(IV) in the solution before the addition of chromium(VI).

A total of six runs were made with different initial concentrations of acetaldehyde. All the kinetic runs were made at 25°.

The calculation for the rate constant of the chromium(VI)-vanadium(IV) system with and without acetaldehyde followed the same method that was explained in detail earlier.<sup>3</sup>

**Analysis of Organic Products.** (a) **Oxidation of Propionaldehyde.** A solution of propionaldehyde (59.1 mmol), vanadium(IV) (12.7 mmol), vanadium(V) (0.954 mmol), and chromium(VI) (3 mmol) in 0.02 *M* perchloric acid was prepared in a 50-ml volumetric flask in an inert atmosphere box. The mixture was allowed to react for about 20 min, removed from the box, and extracted with freshly distilled ether. The ether extract was dried with anhydrous sodium sulfate, concentrated, and analyzed by glpc using a 10 ft by 0.25 in. glass column with 10% Carbowax on 60-80 Chromosorb WAW-DCMS. The only major product found was propionic acid.

Quantitative determination of the product yield was done using the method of internal standardization<sup>12</sup> with nitrobenzene as the internal standard. The method was checked using a synthetic mixture containing propionaldehyde, propionic acid, vanadium(IV), and vanadium(V) in 0.02 *M* perchloric acid, and subjected to work-up procedures identical with those for the oxidation mixture. The amount of propionic acid recovered from the synthetic samples ranged from 62 to 73%. This recovery factor was taken into account when calculating the yield of propionic acid from oxidation experiments.

In order to examine whether additional propionic acid was formed during the analytical procedures, the above experiment was repeated with the same synthetic mixture of propionaldehyde, vanadium(IV), and vanadium(V) in 0.02 *M* perchloric acid, but without added chromic acid. No detectable amount of propionic acid was formed.

(b) **Oxidation of Pivaldehyde.** The oxidation procedures were similar to those of propionaldehyde. In a typical run, the oxida-

tion mixture contained the following reagents: 14.3 mmol of vanadium(IV), 0.763 mmol of vanadium(V), 0.428 g of pivaldehyde, and 3 mmol of chromium(VI) in 50 ml of 0.02 *M* HClO<sub>4</sub>. By glpc analysis, using the peak enhancement method, the oxidation products were found to contain pivalic acid, *t*-BuOH, and a small amount of isobutylene. For the quantitative determination of the yields of pivalic acid and *t*-BuOH, two different extractions were carried out. No quantitative determination was done on the yield of isobutylene.

For the quantitative determination of pivalic acid, freshly distilled ether was used for the extraction of the oxidation mixture. The amount of pivalic acid in the ether solution was determined, using cyclohexanone as internal standard; blank runs were made to determine the recovery factor of the extraction ( $96.25 \pm 1.18\%$ ).

For the determination of *t*-BuOH, 1-octanol (Fisher Certified Reagent) was used for the extraction, and toluene as internal standard; the recovery factor was  $54.02 \pm 1.67\%$ .

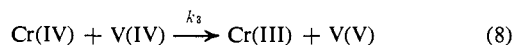
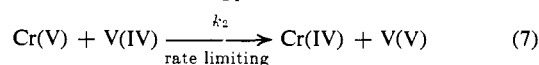
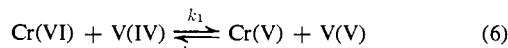
In both cases, blank runs were made which showed that no detectable amount of pivaldehyde was oxidized to the products during the work-up.

## Results and Discussion

### Kinetic Evidence for the Chromium(IV) Oxidation.

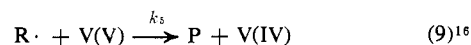
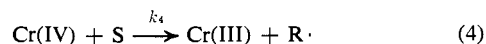
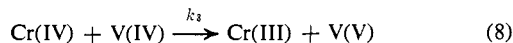
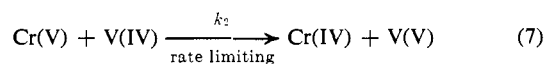
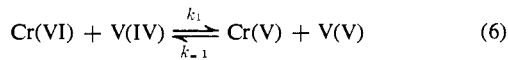
In the oxidation of vanadium(IV) by chromium(VI), the rate-limiting step has been shown to be that involving the reduction of chromium(V) to chromium(IV) (Scheme III).<sup>11</sup> When an aldehyde is introduced into

#### Scheme III



the vanadium(IV)-chromium(VI) system, the yield of vanadium(V) is reduced, indicating that oxidation of the aldehyde takes place. As the oxidation of the aldehyde by chromium(VI) or by vanadium(V) is far too slow to compete with the relatively rapid reduction of chromium(VI) by vanadium(IV),<sup>13</sup> an unstable chromium intermediate must be responsible for the oxidation of the aldehyde. If the aldehyde is reactive only toward chromium(IV), the oxidation will proceed according to Scheme IV, and the overall rate of reduction

#### Scheme IV

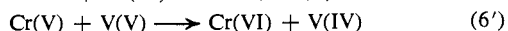
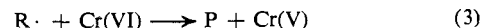


(13) For example, at 25° the second-order rate constant for the chromium(VI) oxidation of acetaldehyde hydrate in 0.5 *M* perchloric acid is  $4.68 \times 10^{-3}$  *M*<sup>-1</sup> sec<sup>-1</sup>,<sup>14</sup> for the vanadium(V) oxidation of propionaldehyde in 1.0 *M* perchloric acid, the rate constant is about  $4 \times 10^{-4}$  *M*<sup>-1</sup> sec<sup>-1</sup>.<sup>15</sup> By contrast, the reduction of chromium(VI) by vanadium(IV) has a rate constant of  $0.563$  *M*<sup>-1</sup> sec<sup>-1</sup>.<sup>11</sup>

(14) J. Rocek and C. S. Ng, *J. Org. Chem.*, **38**, 3348 (1973).

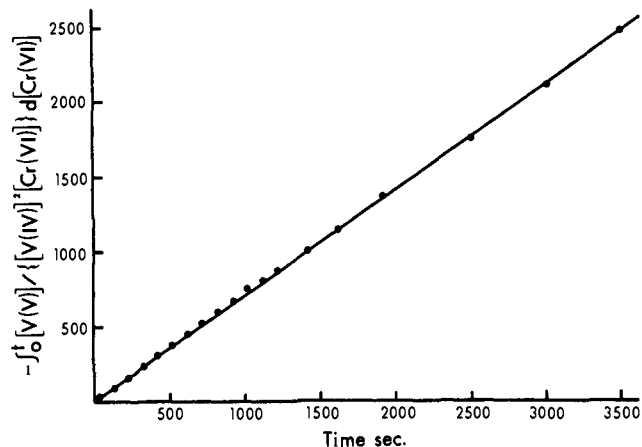
(15) J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 352 (1963).

(16) Or



These two reactions are equivalent to the direct oxidation of the free-radical intermediate by V(V) (reaction 9). The second reaction (6') is the reverse step of the fast reversible oxidation of vanadium(IV) by chromium(VI) (reaction 6), the equilibrium of which lies entirely on the left-hand side.

(12) L. S. Ettre, "The Practice of Gas Chromatography," Interscience, New York, N. Y., 1967, p 401.



**Figure 2.** Integrated rate expression (eq 4) of the chromium(VI)-vanadium(IV) reaction *vs.* time.  $[V(IV)]_0 = 5.27 \times 10^{-4} M$ ;  $[V(V)]_0 = 6.87 \times 10^{-5} M$ ;  $[Cr(VI)]_0 = 3.40 \times 10^{-5} M$ ;  $[HClO_4] = 1.0 \times 10^{-2} M$ .

of chromium(VI) should be no different from that in the absence of the substrate, since the chromium(IV) oxidation of the substrate occurs after the rate-limiting step. If, on the other hand, chromium(V) also oxidizes the substrate, the rate observed in the presence of the substrate will be higher than in its absence. The rate law for Schemes III and IV is

$$-\frac{d[Cr(VI)]}{dt} = k \frac{[Cr(VD)][V(IV)]^2}{[V(V)]} \quad (10)$$

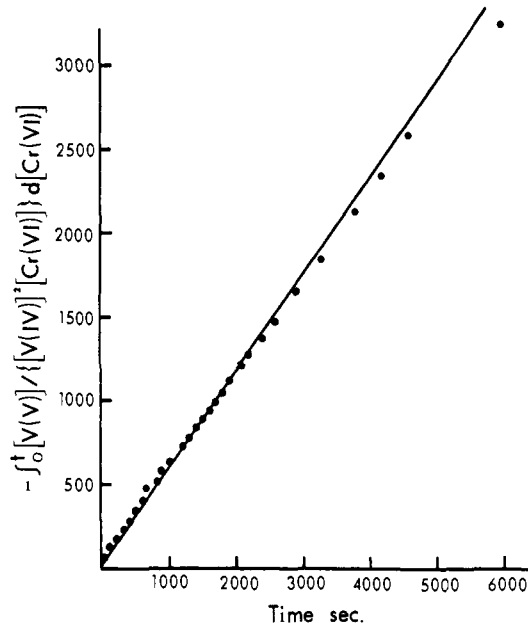
The calculation of the experimental rate constant  $k$  has been described earlier.<sup>3</sup> Figures 2 and 3 are representative plots of  $-\int_0^t ([V(V)]/[V(IV)]^2 [Cr(VI)]) d[Cr(VI)]$  *vs.* time for the chromium(VI)-vanadium(IV) systems with and without acetaldehyde, respectively. The rate constants determined from these plots are given in Table I, and show only small fluctuations in the rate

**Table I.** Kinetics of the Chromium(VI)-Vanadium(IV) System in Water with and without Acetaldehyde<sup>a</sup>

| Initial Concn, $M$    |                      |                        |                         | $k_{exp}, M^{-1} \text{sec}^{-1}$ |
|-----------------------|----------------------|------------------------|-------------------------|-----------------------------------|
| $[V(IV)] \times 10^4$ | $[V(V)] \times 10^5$ | $[Cr(VI)] \times 10^5$ | $[CH_3CHO] \times 10^2$ |                                   |
| 5.25                  | 7.46                 | 3.83                   | 0                       | 0.74                              |
| 5.27                  | 6.87                 | 3.40                   | 0                       | 0.69                              |
| 4.00                  | 22.70                | 3.53                   | 1.70                    | 0.77                              |
| 4.61                  | 18.60                | 3.43                   | 2.55                    | 0.54                              |
| 4.66                  | 17.80                | 3.46                   | 2.55                    | 0.53                              |
| 4.61                  | 18.40                | 3.46                   | 3.40                    | 0.67                              |
| 4.29                  | 19.80                | 3.51                   | 5.10                    | 0.82                              |
| 3.89                  | 23.80                | 3.52                   | 6.79                    | 0.78                              |

<sup>a</sup>  $[HClO_4] = 0.012 M$ .

constant due to experimental errors, but no systematic increase with the increasing concentration of the aldehyde. It is, therefore, safe to conclude that no significant oxidation of acetaldehyde by any oxidant except by chromium(IV) is taking place. Further, the high reactivity of aldehydes toward chromium(IV) strongly suggests that a reaction between the aldehyde and chromium(IV) will take place regardless of the



**Figure 3.** Integrated rate expression (eq 4) of the chromium(VI)-vanadium(IV) reaction *vs.* time in the presence of acetaldehyde.  $[V(IV)]_0 = 5.79 \times 10^{-4} M$ ;  $[V(V)]_0 = 4.87 \times 10^{-5} M$ ;  $[Cr(VI)]_0 = 3.43 \times 10^{-5} M$ ;  $[HClO_4] = 1.0 \times 10^{-2} M$ ;  $[CH_3CHO] = 2.55 \times 10^{-2} M$ .

presence or absence of vanadium. Consequently, the chromic acid oxidation of aldehydes will follow Scheme II rather than Scheme I.

**Products of Oxidation.** The product of the chromium(IV) oxidation of propionaldehyde was identified as propionic acid. In three analyses, the yield of the acid, based on the amount of chromium(VI) available and the reactivity of the aldehyde toward chromium(IV) relative to that of vanadium(IV), was found to be 99.3, 95.6, and 104.9% of the total organic product expected.

In the chromium(IV) oxidation of pivaldehyde, two major products were obtained. They were pivalic acid and *tert*-butyl alcohol. The yields of pivalic acid and *tert*-butyl alcohol, based on the amount of chromium(VI) available and the reactivity of pivaldehyde toward chromium(IV) relative to that of vanadium(IV), are given in Table II.

**Table II.** Yield of Organic Products in the Chromium(IV) Oxidation of Pivaldehyde<sup>a,b</sup>

| Run | % yield of pivalic acid | Run | % yield of <i>tert</i> -butyl alcohol |
|-----|-------------------------|-----|---------------------------------------|
| 1   | 53.9                    | 4   | 33.4                                  |
| 2   | 39.3                    | 5   | 28.0                                  |
| 3   | 47.8                    | 6   | 33.4                                  |
|     | Av 47.0                 |     | Av 31.6                               |

<sup>a</sup> These results were obtained in six independent runs, since pivalic acid and *tert*-butyl alcohol had to be analyzed separately. <sup>b</sup> No quantitative determination was done on the yield of the third product, isobutylene.

**Relative Reactivity of the Chromium(IV) Oxidation of Aliphatic Aldehydes.** In our studies in the chromium(IV) oxidation of alcohols, we have shown that for systems following Scheme IV, the yield of va-

Table III. Rate of Oxidation of Aliphatic Aldehydes Relative to That of Vanadium(IV) by Chromium(VI)

| Aldehyde  | $K_d$                  | $(k_4/k_3)_A$       | $(k_4/k_3)_H$        | $(k_4/k_3)_C$ |
|---|------------------------|---------------------|----------------------|---------------|
| HCHO  | 0.000550 <sup>19</sup> | 0.205 ± 0.006       | 0.205                | 745.9         |
| CH <sub>3</sub> CHO                                 | 0.67 <sup>20,21</sup>  | 0.123 ± 0.006       | 0.205                | 0.306         |
| CH <sub>3</sub> CH <sub>2</sub> CHO                 | 1.4 <sup>22</sup>      | 0.172 ± 0.007       | 0.413                | 0.294         |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO | 2.1 <sup>22</sup>      | 0.20 ± 0.0          | 0.620                | 0.296         |
| (CH <sub>3</sub> ) <sub>3</sub> CCHO                | 4.1 <sup>23</sup>      | 0.321 ± 0.013       | 1.64                 | 0.399         |
| ClCH <sub>2</sub> CHO                               | 0.027 <sup>24</sup>    | 0.0179 ± 0.0009     | 0.0184               | 0.681         |
| Cl <sub>2</sub> CHCHO                               |                        | 0.00542 ± 0.00002   | 0.00542 <sup>a</sup> |               |
| Cl <sub>3</sub> CCHO                                | 0.000036 <sup>22</sup> | 0.0016 <sup>b</sup> | 0.0016               | 45            |
| CH <sub>3</sub> CH <sub>2</sub> CDO                 |                        | 0.104 ± 0.002       |                      |               |
| (CH <sub>3</sub> ) <sub>3</sub> CCDO                |                        | 0.156 ± 0.001       |                      |               |

<sup>a</sup> No value of the hydration equilibrium constant for Cl<sub>2</sub>CHCHO could be found in the literature. It is assumed here that this value lies somewhere between those for ClCH<sub>2</sub>CHO and Cl<sub>3</sub>CCHO, thus making  $(k_4/k_3)_H \approx (k_4/k_3)_A$ . <sup>b</sup> The reactivity of Cl<sub>3</sub>CCHO toward Cr(IV) was too slow for accurate determination of  $k_4/k_3$ . The value here is an approximate one.

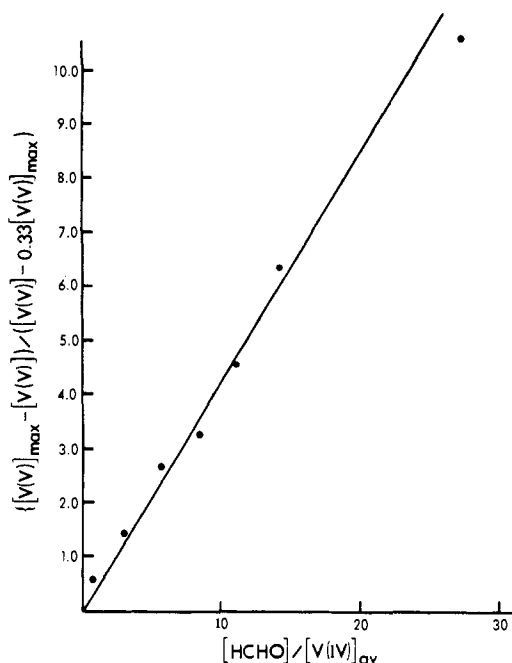


Figure 4. Determination of the relative rate of the chromium(IV) oxidation of formaldehyde.

vanadium(V) may be expressed as a function of the substrate and vanadium(IV) concentrations<sup>3</sup>

$$\frac{[V(V)]_{\max} - [V(V)]}{[V(V)] - 0.33[V(V)]_{\max}} = \frac{k_4[S]}{k_3[V(IV)]_{av}} \quad (11)$$

where  $[V]_{\max}$  = the yield of vanadium(V) in the absence of substrate,  $[V]$  = yield of vanadium(V) in the presence of substrate,  $[S]$  = concentration of substrate which may be regarded as constant,  $[V(IV)]_{av}$  = average value of the initial and final concentrations of vanadium(IV),  $k_3$  = rate constant for the chromium(IV) oxidation of vanadium(IV), and  $k_4$  = rate constant for the chromium(IV) oxidation of the substrate.

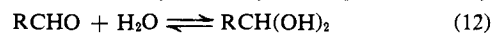
Using this approach to the results obtained in the present study led to good straight lines (e.g., Figure 4), from which the values of  $k_4/k_3$  could be determined.

The aldehyde concentration used in calculating the  $k_4/k_3$  values according to eq 1 was the total analytical concentration. It is well known that aliphatic aldehydes in aqueous solutions are partially hydrated.<sup>17</sup>

In order to gain an understanding of the reaction mechanism, it was essential to decide whether the free

aldehyde form or the aldehyde hydrate reacts with chromium(IV).<sup>18</sup> The following approach was used.

The hydration of aldehydes may be represented by



$$K_d = [RCHO]/[RCH(OH)_2] \quad (13)$$

If the total concentration of the aldehyde,  $[A]$ , is used in the calculation of eq 11, then

$$\frac{[V(V)]_{\max} - [V(V)]}{[V(V)] - [V(V)]_{\max}/3} = (k_4/k_3)_A \frac{[A]}{[V(IV)]_{av}} \quad (11)$$

Let

$$Q = \frac{[V(V)]_{\max} - [V(V)]}{[V(V)] - [V(V)]_{\max}/3}$$

then

$$(k_4/k_3)_A = \frac{Q}{[A]/[V(IV)]_{av}} \quad (14)$$

If the oxidation is assumed to go through the hydrated form, then

$$(k_4/k_3)_H = \frac{Q}{[RCH(OH)_2]/[V(IV)]_{av}} \quad (15)$$

Now

$$[A] = [RCH(OH)_2] + [RCHO] \quad (16)$$

and

$$[RCHO] = K_d[RCH(OH)_2] \quad (17)$$

therefore

$$[A] = K_d[RCH(OH)_2] + [RCH(OH)_2] \quad (18)$$

and

$$[RCH(OH)_2] = [A]/(K_d + 1) \quad (19)$$

Substituting this expression for  $[RCH(OH)_2]$  in eq 15

$$(k_4/k_3)_H = \frac{Q}{[A]/[V(IV)]_{av}} (K_d + 1) \quad (20)$$

Hence if the reaction goes through the hydrate

$$(k_4/k_3)_H = (k_4/k_3)_A (K_d + 1) \quad (21)$$

In a similar manner, it may be shown that if the reaction goes through the carbonyl form,  $(k_4/k_3)_C$  may be obtained from

$$(k_4/k_3)_C = (k_4/k_3)_A (1 + 1/K_d) \quad (22)$$

In Table III are shown the three values of  $k_4/k_3$  of the

(18) Cf. J. Roček in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, London, 1966, p 461.

(17) R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

Table IV. Rate of Oxidation of Aliphatic Aldehydes Relative to That of Acetaldehyde by Chromium(IV)

| Aldehyde R-CHO                                       | Substituent R                                   | $\sigma^*$ | $(k/k_{\text{CH}_3\text{CHO}})_A$ | $(k/k_{\text{CH}_3\text{CHO}})_H$ | $(k/k_{\text{CH}_3\text{CHO}})_C$ |
|--|---|------------|-----------------------------------|-----------------------------------|-----------------------------------|
| H-CHO  | H   | +0.490     | 1.66                              | 1.00                              | 1220                              |
| CH <sub>3</sub> -CHO                                 | CH <sub>3</sub>                                 | 0.000      | 1.00                              | 1.00                              | 1.00                              |
| CH <sub>3</sub> CH <sub>2</sub> -CHO                 | CH <sub>3</sub> CH <sub>2</sub>                 | -0.100     | 1.40                              | 2.01                              | 0.96                              |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -CHO | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> | -0.115     | 1.63                              | 3.02                              | 0.97                              |
| (CH <sub>3</sub> ) <sub>3</sub> C-CHO                | (CH <sub>3</sub> ) <sub>3</sub> C               | -0.300     | 2.61                              | 7.98                              | 1.30                              |
| ClCH <sub>2</sub> -CHO                               | ClCH <sub>2</sub>                               | +1.050     | 0.146                             | 0.0898                            | 2.22                              |
| Cl <sub>2</sub> CH-CHO                               | Cl <sub>2</sub> CH                              | +1.940     | 0.044                             | 0.0264                            |                                   |
| Cl <sub>3</sub> C-CHO                                | Cl <sub>3</sub> C                               | +2.65      | 0.013                             | 0.0079                            | 150                               |

aldehydes,  $(k_4/k_3)_A$ ,  $(k_4/k_3)_H$ , and  $(k_4/k_3)_C$ , representing the relative rate based on: (1) the total aldehyde concentration, (2) the hydrate concentration, and (3) the concentration of the carbonyl form, respectively. The table also lists the values of the hydration equilibrium,  $K_d$ ,<sup>19-24</sup> which were used to calculate  $(k_4/k_3)_H$  and  $(k_4/k_3)_C$  from  $(k_4/k_3)_A$ .

Table IV lists the rate of chromium(IV) oxidation of the aldehydes relative to that of acetaldehyde obtained by dividing the  $k_4/k_3$  of the aldehyde by that of acetaldehyde. The table also lists the values of the Taft's polar substituent constants,  $\sigma^*$ ,<sup>25</sup> of the aldehydes. A plot of  $\log(k/k_{\text{CH}_3\text{CHO}})_H$  vs.  $\sigma^*$  gives a reasonably good straight line (Figure 5; correlation coefficient 0.98, standard deviation 0.26) with a slope of  $-0.96$ . On the other hand, the correlation of  $\sigma^*$  with  $\log(k/k_{\text{CH}_3\text{CHO}})_C$  is much less satisfactory. The main deviation is observed for formaldehyde which appears to be over 1000 times more reactive than would be predicted from the  $\sigma^*-\rho^*$  plot based on the other aldehydes. When the value for formaldehyde is dropped, a reasonable straight line (correlation coefficient 0.95, standard deviation 0.29) giving a value of  $\rho^* = 0.72$  may be obtained.

As in our studies on the chromium(VI) oxidation of aliphatic aldehydes,<sup>14</sup> the case of formaldehyde is of particular interest. If one assumes that the aldehyde reacts *via* the hydrated form, a value of  $(k/k_{\text{CH}_3\text{CHO}})_H$  is obtained, which compares well with the reactivities of other aldehydes. On the other hand, if one assumes that formaldehyde is oxidized directly *via* the carbonyl form, one would have to assume that formaldehyde is over 1000 times more reactive than the other aldehydes. This finding makes a mechanism consisting of a direct hydrogen abstraction from the free aldehyde very unlikely.

**Role of the Enol Form.** In the oxidation of enolizable aldehydes by one-equivalent oxidants like vanadium(V) and manganese(III) pyrophosphate, it has been proposed that the oxidation goes through the enol form of the aldehyde.<sup>15, 18, 26</sup> In contrast, no evidence could be found for the involvement of the enol in the chromium(IV) oxidation of the aliphatic aldehydes. If the enol were involved, nonenolizable aldehydes should be very unreactive, as is true in the oxidations with vanadium(V) and manganese(III) pyrophosphate; however,

(19) P. Valenta, *Collect. Czech. Chem. Commun.*, **25**, 853 (1960).

(20) R. P. Bell and J. C. Clunie, *Trans. Faraday Soc.*, **48**, 439 (1952).

(21) E. Lombardi and P. B. Sogo, *J. Chem. Phys.*, **32**, 635 (1960).

(22) L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5217 (1963).

(23) P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, **89**, 749 (1967).

(24) P. Federlin, *C. R. Acad. Sci.*, **235**, 44 (1952).

(25) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 619.

(26) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 440 (1953).

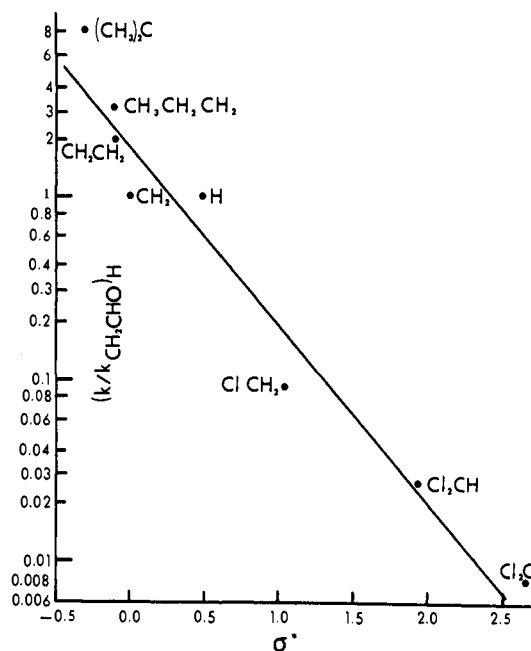


Figure 5. Relative rate of chromium(IV) oxidation of aliphatic aldehyde hydrates,  $\text{RCH}(\text{OH})_2$ , vs.  $\sigma^*$  values.

formaldehyde reacted at a rate comparable to that of acetaldehyde and propionaldehyde, and pivaldehyde was several times more reactive than acetaldehyde. The oxidation of trichloroacetaldehyde occurred more slowly, but this was due to the electron-withdrawing effect of the trichloro group rather than to the non-enolizability of the compound, as was evident from its fit in the  $\sigma^*-\rho^*$  plot (Figure 5). Also, if the oxidation took place *via* the enol form,  $\alpha$ -hydroxypropionaldehyde should be the product in the oxidation of propionaldehyde. Since the yield of propionic acid in the oxidation was close to 100%, only a very small amount, if any, of  $\alpha$ -hydroxypropionaldehyde was formed. Thus, it seems that the enol form may be safely excluded in considering the chromium(IV) oxidation of aldehydes.

**Mechanism of Oxidation.** In discussing the mechanism of the chromium(IV) oxidation of aldehydes, the following observations have to be taken into account: (1) the oxidation exhibits a moderate primary isotope effect; (2) the reaction proceeds through an aldehyde hydrate or an aldehyde hydrate-like intermediate; (3) there is a close similarity between the chromium(IV) oxidation of aldehyde hydrates and of alcohols.

The magnitude of the primary deuterium isotope effect observed in the chromium(IV) oxidation of propionaldehyde and pivaldehyde is given in Table V. For comparison, the values for primary isotope effects obtained in the chromium(IV) oxidation of isopropyl

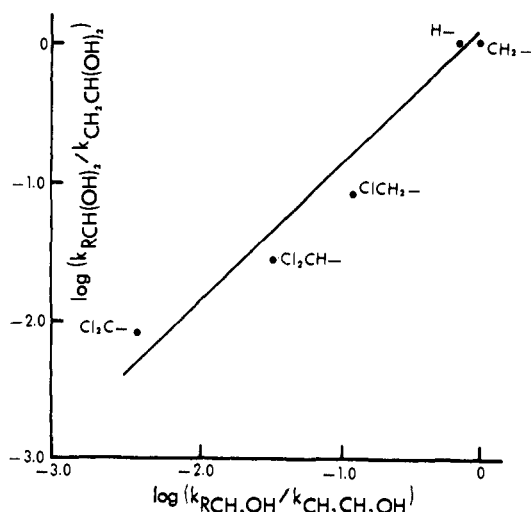


Figure 6. Comparison of chromium(IV) oxidation rates of aldehydes and primary alcohols.

Table V. Isotope Effects in One-Electron Oxidations

| Substrate | Oxidant  | $k_H/k_D$  |
|-----------|--|--|
|           | Ce <sup>IV</sup><br>Co <sup>III</sup><br>Mn <sup>III</sup> | 1.9 <sup>a</sup><br>1.7 <sup>b</sup><br>1.6 <sup>c</sup> |
|           | Cr <sup>IV</sup>   | 1.9 <sup>3</sup>   |
|           | Cr <sup>IV</sup>   | 2.4 <sup>d</sup>   |
|           | Co <sup>III</sup>  | 2.3 <sup>e</sup>   |
|           | Cr <sup>IV</sup>   | 1.7  |
|           | Cr <sup>IV</sup>   | 2.1  |

<sup>a</sup> J. S. Littler, *J. Chem. Soc.*, 4135 (1959). <sup>b</sup> D. G. Hoare and W. A. Waters, *ibid.*, 965 (1962). <sup>c</sup> J. S. Littler, *ibid.*, 2190 (1962). <sup>d</sup> P. Müller and J. Roček, to be published. <sup>e</sup> T. A. Cooper and W. A. Waters, *J. Chem. Soc.*, 1538 (1964).

alcohol and of cycloheptatriene, as well as values available in the literature for the oxidation of cyclohexanol and *m*-nitrobenzaldehyde by one-equivalent oxidants, are included. The magnitude of the isotope effects observed in this study thus agrees well with those for similar hydrogen abstraction reactions studied earlier.

The substituent effect on the aldehyde hydrate oxidation rate ( $\rho^* = -0.96$ ) is similar to those observed in many other hydrogen atom abstraction reactions (Table VI), and supports the assumption that a hydrogen atom is lost from the aldehyde hydrate in the rate-limiting step. If the oxidation involved direct hydrogen atom abstraction from the free aldehyde, then the reaction constant,  $\rho^*$ , based on the free aldehyde,

Table VI. Hammett Relations for Hydrogen Atom Abstraction Reactions

| Type of compd   | Temp, °C | Abstracting Agent                   | $\rho$ | Ref      |
|---|----------|-------------------------------------|--------|----------|
| Toluenes  | 40       | (CH <sub>3</sub> ) <sub>3</sub> CO· | -0.83  | <i>a</i> |
|   | 40       | (CH <sub>3</sub> ) <sub>3</sub> CO· | -0.76  | <i>b</i> |
|   | 40       | Cl·                                 | -0.66  | <i>c</i> |
|   | 80       | Cl <sub>2</sub> C·                  | -1.46  | <i>d</i> |
|   | 80       | Br·                                 | -1.36  | <i>e</i> |
|   | 136      | (CH <sub>3</sub> ) <sub>2</sub> N·  | -1.08  | <i>f</i> |
| 1-Substituted adamantanes (abstraction of bridgehead H) | 40       | Cl <sub>2</sub> C·                  | -0.40  | <i>g</i> |
|   | 40       | Br·                                 | -0.59  | <i>h</i> |
| Cumenes   | 70       | Br·                                 | -0.38  | <i>i</i> |
|   | 70       | Cl <sub>2</sub> C·                  | -0.89  | <i>i</i> |
| Diphenylmethanes  | 80       | Br·                                 | -0.93  | <i>j</i> |
|   | 77       | Br·                                 | -0.97  | <i>k</i> |
| Benzaldehydes   | 40       | NO <sub>2</sub>                     | -1.10  | <i>l</i> |
| Primary alcohols  | 25       | Cr <sup>IV</sup>                    | -0.85  | 3        |

<sup>a</sup> C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6113 (1960). <sup>b</sup> R. D. Gilliom and J. R. Howles, *Can. J. Chem.*, **46**, 2752 (1968). <sup>c</sup> G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964). <sup>d</sup> E. S. Huyser, *ibid.*, **82**, 394 (1960). <sup>e</sup> R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963). <sup>f</sup> C. J. Michejda and W. P. Hoss, *ibid.*, **92**, 6298 (1970). <sup>g</sup> P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *ibid.*, **90**, 4122 (1968). <sup>h</sup> G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruh, *Tetrahedron Lett.*, 833 (1969). <sup>i</sup> G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968). <sup>j</sup> T. P. Low and K. H. Lee, *J. Chem. Soc. B*, 535 (1970). <sup>k</sup> S. S. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **35**, 944 (1970). <sup>l</sup> T. Yoshida and K. Namba, *Kogyo Kagaku*, **29**, 353 (1968).

should have a value of around  $-1$ , instead of  $+0.72$ , as found in the present study. This argument is supported by the finding that the  $\rho$  value for the nitrogen dioxide abstraction of a benzylic hydrogen atom in substituted benzaldehydes is  $-1.1$ ; since the reactions were carried out in benzene, no hydrates could be present.<sup>27</sup> Also, hydrogen atom abstraction by trifluoromethyl radicals from pentafluorobenzaldehyde and trifluoroacetaldehyde in the gas phase requires higher activation energy than from benzaldehyde<sup>28</sup> and acetaldehyde,<sup>29</sup> respectively.

The similarity between the oxidation of aldehyde hydrates and alcohols is borne out not only by the isotope effects, but also in Figure 6, which gives a direct comparison of the relative oxidation rates for pairs of corresponding aldehyde hydrates and primary alcohols (slope 1.1, correlation coefficient 0.98, standard deviation 0.13).<sup>30</sup> We therefore assume that the chromium(IV) oxidation of aldehydes proceeds through the same type of reaction intermediate, a coordination compound formed from the aldehyde hydrate and chromium(IV), which was earlier proposed for the chromium(IV) oxidation of alcohols.<sup>3</sup>

All available observations can be accommodated by the mechanism given in Scheme V, which closely resembles that proposed earlier for the chromium(IV) oxidation of alcohols.

Further support for a mechanism involving hydrogen

(27) T. Yoshida and K. Namba, *Kogyo Kagaku*, **29**, 353 (1968).

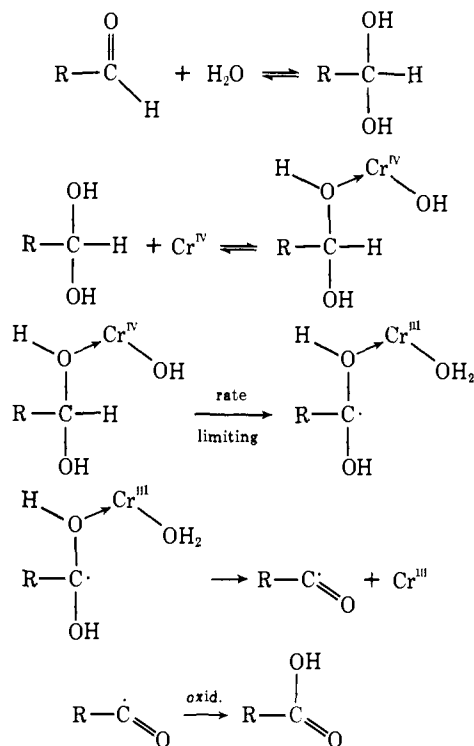
(28) J. R. Majer, S.-A. M. A. Naman, and J. C. Robb, *Trans. Faraday Soc.*, **65**, 3295 (1969).

(29) R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1465 (1957).

(30) Kemp and Waters<sup>31</sup> noted earlier that the oxidation of formaldehyde with several oxidants closely resembles the oxidation of alcohols, and concluded therefore that formaldehyde reacted in its hydrated form.

(31) T. J. Kemp and W. A. Waters, *Proc. Roy. Soc., Ser. A*, **274**, 480 (1963).

Scheme V



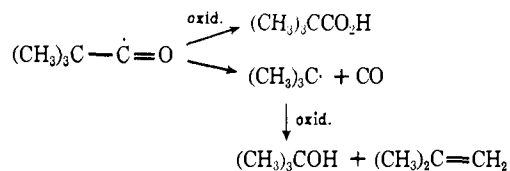
atom abstraction leading to a free radical can be derived from the trapping of acyl radicals, as 2-acyl-benzothiazoles, in the chromic acid oxidation of aldehydes.<sup>32</sup>

The formation of both pivalic acid and *tert*-butyl alcohol and isobutylene indicates that the free-radical

(32) T. Caronna, R. Galli, V. Malatesta, and F. Minisci, *J. Chem. Soc. C*, 1747 (1971).

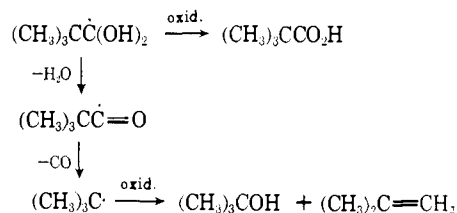
intermediate can react by oxidation and decarbonylation at comparable rates. Whether it is the same radical which in part decarbonylates and in part undergoes oxidation (Scheme VI), or whether two different free-

Scheme VI



radical intermediates are involved (Scheme VII), cannot

Scheme VII



be decided at this point. In Scheme VII it is suggested that the radical may be formed in the hydrated form, which then is either oxidized to the acid or undergoes dehydration followed by rapid decarbonylation.

A similar observation has been made in the manganese(III) acetate oxidation of pivaldehyde in glacial acetic acid, in which carbon monoxide, isobutylene, and isobutane were isolated in moderate yields.<sup>33</sup>

**Acknowledgments.** The support of this work by the National Science Foundation is gratefully acknowledged.

(33) G. I. Nikishin, M. G. Vinogradov, and S. P. Verenchikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1835 (1969).