TABLE III

CONDUCTANCE OF ACETIC ACID–WATER MIXTURES

Acetic acid, %	κ_0	Equiv. [$NaClO_4$]	K
100			2.5×10^{-13}[6]
95	4.67×10^{-6}	2.0×10^{-4}	4.0×10^{-8}
91	1.11×10^{-5}	4.0×10^{-4}	1.6×10^{-7}
85	4.50×10^{-5}	15.4×10^{-4}	2.4×10^{-6}

dielectric constant will make the formation of ions relatively less favorable.

Acknowledgment.—We wish to thank the National Science Foundation for their support of this work.

Experimental

H_0 Measurements.—The spectrophotometric data were obtained using a Beckman DU spectrometer and 1-cm. cells. The acetic acid was purified by distillation from chromic acid under reduced pressure. The acetic acid water mixtures were made up by weight. A set of typical data is shown in Table IV.

Conductance Measurements.—The conductance was measured using a Leeds and Northrup Jones bridge, and a cell of the design suggested by Jones.[7] The cell constant was determined using a potassium chloride solution, and had a value of 0.2195.

TABLE IV

H_0 DETERMINATION IN 85% ACETIC ACID

[p-Nitroaniline] $\times 10^5$	[$HClO_4$]	Optical density 380 mμ	378 mμ	376 mμ	374 mμ	372 mμ	370 mμ	[BH^+]/[B]	H_0
48.5	0.300	0.321	0.327	0.331	0.335	0.339	0.340	21.5	−0.34
48.5	.225	.448	.453	.460	.463	.465	.467	14.7	− .18
24.3	.150	.339	.344	.348	.349	.350	.352	9.03	.03
14.6	.075	.384	.387	.392	.394	.395	.394	4.23	.36
9.70	.045	.377	.382	.385	.385	.386	.385	2.52	.59
9.70	.030	.494	.500	.504	.505	.506	.505	1.66	.76
9.70	.015	.694	.701	.708	.709	.710	.707	0.902	1.03
4.85	0.3 M NaOAc	.657	.666	.669	.670	.671	.669		
4.85	BH^+	.0026	.0031	.0034	.0034	.0036	.0038		

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(6) I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1007 (1934).

(7) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Kinetics of the Chromic Acid Oxidation of Benzaldehyde

BY KENNETH B. WIBERG AND THEODORE MILL[1]

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The kinetics of the chromic acid oxidation of benzaldehyde has been found to have the rate law: $V = k[RCHO][HCrO_4^-]h_0$. The reaction was found to have a deuterium isotope effect of 4.3, and manganous ion was found to markedly decrease the rate of reaction. Electron-withdrawing groups were found to accelerate the reaction. These data suggest that a mechanism which is analogous to that for the permanganate oxidation of benzaldehyde may be operative.

Introduction

In a previous investigation,[2] the mechanism of the permanganate oxidation of benzaldehyde was studied. The possibility of a similarity in reaction between permanganate and chromic acid has prompted an investigation of the oxidation of benzaldehyde by the latter reagent. This reaction has been studied by Lucchi,[3] but his results are not sufficiently detailed to be a basis for the formulation of a mechanism for the reaction.

The reaction between benzaldehyde and chromic acid proceeds very slowly in water solution. However, in acetic acid–water mixtures the reaction proceeds at a reasonable rate. The increased solubility of benzaldehyde in this medium is also a convenience. The reaction was studied in 91% (by weight) acetic acid since this mixture gave a convenient rate of reaction and is similar to mixtures commonly used in synthetic work.

Experimental

Reagents.—Benzaldehyde was purified immediately before use by two successive distillations in a nitrogen atmosphere. In some cases the benzaldehyde was purified *via* the bisulfite addition compound, but in no case was any difference in rate observed using material purified by the two methods. The solid aldehydes, p-chlorobenzaldehyde, p-nitrobenzaldehyde and m-nitrobenzaldehyde were recrystallized from an ethanol–water mixture and then sublimed twice at 2 mm. pressure at a temperature slightly above their melting points. The liquid aldehydes were distilled under reduced pressure shortly before they were used. Benzaldehyde-d_1 was prepared as described previously.[4]

All of the solid inorganic reagents were reagent grade and were converted to the anhydrous form before making up solutions. Chromium trioxide was recrystallized from water before use. The perchloric acid was obtained as a 71% solution and was a reagent grade. The acetic acid was purified by heating reagent grade material with potassium dichromate and sulfuric acid followed by distillation under reduced pressure. When it was distilled at atmospheric pressure it was found to obtain a small amount of a

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(1) Taken from a thesis submitted by T. Mill to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1957.

(2) K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

(3) E. Lucchi, *Bull. sci. facolta chim. ind. Bologna*, **I**, 208, 318 (1940); **II**, 165, 175 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941).

(4) K. B. Wiberg, THIS JOURNAL, **76**, 5371 (1954).

substance which reduced chromic acid and interfered seriously with the spectrophotometric investigations.

The solvent used for all the experiments was prepared by adding 38 liters of purified acetic acid (containing 0.24% water by Karl Fischer titration) to 3830 ml. of water at 25°. Using the known densities of acetic acid and water this may be calculated to give a solvent containing 91.0% acetic acid by weight. This quantity of solvent was sufficient for all of the kinetic and spectrophotometric determinations.

Kinetic Method.—The apparatus used for the kinetic runs consisted of a 250-ml. or a 125-ml. round-bottom flask to which two 15-ml. diameter tubes were sealed at the sides of the center neck. One served as an entrance for nitrogen while the other was used to remove aliquots during the run. Normally nitrogen by-passed the flask through a mercury valve, but when an aliquot was removed the nitrogen passed through the flask at a very gentle rate.

Solutions for runs were made up from stock solutions to three times the desired initial concentration for each run. Before initiating a run the reaction flask was swept with nitrogen and the solutions were thermally equilibrated. Equal, arbitrary volumes of each of the three solutions (chromic acid, benzaldehyde and perchloric acid–sodium perchlorate) used in every run were then introduced into the flask. The zero time of the reaction was noted when half of the third solution was in the flask. Aliquots were removed at various intervals and analyzed for chromium (or benzaldehyde) as described below.

The standard solutions of the solid reagents were made up either by direct weighing or approximate weighing followed by analysis of the solution. All solutions were prepared and analyzed at room temperature. Volumetric transfer pipets of various sizes were calibrated with the solvent by weighing the delivered volume and calculating the volume from the density. No corrections for concentration changes were made in the solution used at 30°, but a correction of 1.5% was made for concentrations at 60°.

Solutions of known concentration of benzaldehyde could be made up by delivering a volume from a calibrated pipet. However, there was no difficulty in weighing benzaldehyde directly, and this was done in all cases. An approximate volume of freshly distilled aldehyde was added to a tared volumetric flask containing some solvent and it was then reweighed. The same procedure could be used for all the liquid aldehydes. Solid aldehydes were weighed directly. Analysis of benzaldehyde solution, both standard and kinetic solutions containing chromium(VI) and perchloric acid, were carried out as described below.

Perchloric acid in the acetic acid–water solvent was made so that the water constituted 9% by weight of the total solvent. In a typical preparation some 400 ml. of purified glacial acetic acid was mixed with about 60 ml. of commercial, 70% perchloric acid and this mixture was reweighed. Doubly distilled water was added from the volume buret in an amount sufficient to constitute 9% by weight of the solvent, the water in the perchloric acid being taken into account. This perchloric acid was standardized by potentiometric titration. A 1- or 2-ml. aliquot was mixed in a titration vessel with about 30 ml. of glacial acetic acid, and 1 ml. of acetic anhydride was added to remove water in the sample. After the reaction was complete and the solution had cooled it was titrated with 0.500 M sodium acetate in glacial acetic acid using a glass electrode with a silver–silver chloride reference electrode and a Beckman *p*H meter. The end-point was determined graphically and was precise to 1%. These stock acid solutions were quite stable showing no change in titer over several months of standing. The reference electrode was made simply by attaching two silver wires to the poles of a 6-volt dry cell and immersing the ends of the wire in 3 M hydrochloric acid until the anode was well coated with silver chloride.

Stock Cr(VI) solutions were made up either from chromium trioxide or sodium dichromate. The chromium trioxide solutions decomposed slowly because of the slight amount of acid present and were abandoned in favor of dichromate. The standardization of the Cr(VI) solutions was carried out iodometrically.

Analytical Method.—Both the stock chromium(VI) solutions and the aliquots from the rate runs were analyzed iodometrically. Potassium dichromate in water was used as the primary standard. This method is subject to considerable error associated with the air oxidation of iodide ion in acidic medium. Difficulty might also be associated with the use of solutions containing considerable acetic acid. A number of experiments were therefore performed in order to determine the conditions for optimum accuracy and precision.

The final procedure adopted consisted of adding a known volume (5 ml.) of chromium(VI) solution in acetic acid to 20 ml. of 0.3 M potassium iodide containing 0.3 g. of sodium bicarbonate. Then 2 ml. of 6 M sulfuric acid was added and the solution was set aside for 10 minutes. It was diluted with 70 ml. of water and titrated with thiosulfate. The standardization of the thiosulfate was accomplished in the same manner with standard potassium dichromate. In this case, an amount of acetic acid equal to that introduced in the unknown chromium(VI) solution was added. Solutions varying from 0.5 to 0.001 M could be analyzed by this procedure by varying the normality of the thiosulfate so as to give a convenient titer.

The error introduced by air oxidation of iodide ion under these conditions was negligible with chromium(VI) solutions of concentration greater than 0.003 M. Below this concentration, correction for air oxidation was applied, but did not affect the value of the rate constants by more than 3%, the experimental error. The instability of the dilute (0.01 N) thiosulfate solutions made it necessary to restandardize frequently during the analyses.

The benzaldehyde concentration in both the stock solutions and in the aliquots from the kinetic runs was determined gravimetrically as the 2,4-dinitrophenylhydrazone.[5] A sample which would give about 120 mg. of the phenylhydrazone was taken in each case. Duplicate samples agreed within 1% and agreed within 1.5% with the values calculated from the stock solutions. The aliquots from the kinetic runs were quenched by addition to an arsenite solution before analysis.

Determination of Monomer–Dimer Equilibrium Constant.—All spectral measurements were taken with Beckman DU quartz spectrometer. The instrument was equipped with a cell compartment designed to hold cells up to 10 cm. in length. The compartment was thermostated at 25.1° with thermospacers. The measurements were made at 25° rather than 30° for reasons of convenience and in keeping with the practice of measuring thermodynamic quantities at this temperature. No significant difference was found in measuring some solutions at 30° as compared to the value at 25°. Measurements were made in the region from 380 to 410 mμ at 10-mμ intervals, a tungsten lamp being used as a source.

The objective in this study was an over-all precision of 3% for optical density determinations of Cr(VI) solutions ranging in concentration from 1.58×10^{-2} to 10^{-4} molar using cells of path lengths of 0.098 to 10.001 cm. This precision required keeping errors associated with cell alignment, internal reflection and cell corrections to a minimum. The recommendations of Beckman[6] with respect to the handling of the cells and the instrument were followed.

Before the solutions were prepared and spectral readings taken, all the glassware and optical cells were cleaned with chromic acid and sulfuric acid, rinsed with water and solvent and then dried. Dust was excluded as much as possible. The spectrometer, tungsten lamp and charger were turned on two hours before using and allowed to reach electrical stability. The cell compartment was thermostated continuously. A pair of cells was placed in the compartment and taped to the holder to prevent movement while cells were being moved in and out of the light beam.

All transfers of liquids in and out of cells were accomplished with hypodermic syringes fitted with Teflon adapters and glass needles. For the very short cells, 0.5 and 0.098 cm., stainless steel needles were used and these were washed after each transfer; stainless steel is attacked rather rapidly by these perchloric acid solutions. So long as a pair of cells were being used, they remained in the cell compartment.

Cell corrections for each pair of cells were obtained by filling both cells with a blank solution consisting of the solvent 0.200 M in sodium perchlorate and 0.100 M in perchloric acid. The solution is transparent in this region of the spectrum; the highest optical density observed (against the air) was 0.010 in a 10-cm. cell. Both the cell corrections

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[5] S. Siggia, "Quantitative Organic Analysis by Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 31–32.

[6] A. O. Beckman, *Anal. Chem.*, **25**, 869 (1953).

and the spectra were determined using a slit width of 0.08 mm. Cell corrections were determined starting at 380 mμ and going up to 410 mμ. At 400 mμ a filter was inserted in the beam and readings were taken before and after insertion of the filter. These values were the same in most cases. The procedure was repeated with the same solutions starting with 380 mμ again.

The long cells had rather high corrections (+0.010) and these changed quite capriciously from one blank solution to another, but did not change appreciably from one wave length to another. At least ten values for each given blank solution at each wave length were taken for the 10- and 5-mm. cells. The shorter cells had small corrections (±0.002) which were more reproducible. The average of readings at a wave length was used as the correction factor for the chromium solutions.

All chromium solutions were prepared from two stock solutions, 0.00318 and 0.0316 *M*. When used they were analyzed daily for concentration. An aliquot stock solution was diluted with solvent to twice the desired concentration and then diluted 1:1 with the solution 0.400 *M* in sodium perchlorate and 0.200 *M* in perchloric acid.[7]

The solutions were thermostated at 25° before insertion into the optical cells. The solution cell was rinsed with some of the chromium solution until constant optical density values could be obtained. The measurements were made with three or four samples of solution and in some cases duplicate solutions were made up. The average of some eight optical density values at each wave length was computed and the average cell correction was then applied. This corrected density value was used for the calculation purposes.

Experiments using Manganese(II).—Manganous perchlorate was prepared in two ways. Anhydrous reagent grade manganous acetate was evaporated carefully with slightly more than one equivalent of 70% perchloric acid until white anhydrous perchloric acid was formed. The solid was twice recrystallized from dilute aqueous perchloric acid and the manganous perchlorate was dried at 5-μ pressure and 150°. The perchlorate salt very tenaciously retains its water of hydration. The dried salt was weighed approximately and made up to volume with the solvent. Aliquots were analyzed for manganese content by oxidation with bismuthate to permanganate, reduction with excess ferrous sulfate and back titration with permanganate. The other method was to dissolve an accurately weighed portion of manganous acetate in the acetic acid–water solvent and add to it a calculated amount of standard stock perchloric acid. Manganese analyses were made as described above. Titration with sodium acetate indicated only a negligible amount of the excess perchloric acid was present. In those runs where manganese was to be added, the manganous ion was always added with the perchloric acid to avoid the formation of a chromium(IV)–manganese(II) complex.

Anhydrous magnesium perchlorate was the commercial Anhydrone which was used without further purification. A sample was weighed out and made up to volume. A peculiar initial acceleration was found in runs containing magnesium perchlorate and this prompted the check of the purity by a blank. A solution of 0.06 *M* in magnesium perchlorate, 0.005 *M* in chromium(VI), and 0.200 *M* in perchloric acid showed no loss in oxidizing power after standing four hours.

Results and Discussion

Before determining the rate law for the chromic acid oxidation of benzaldehyde it was necessary to examine the stoichiometry of the reaction. One would presume the reaction to be

$$3RCHO + 2CrO_3 + 6H^+ \longrightarrow 3RCOOH + 2Cr^{+3} + 3H_2O$$

A reaction mixture containing equivalent amounts of benzaldehyde and chromic acid (based on the above stoichiometry) was prepared and the disappearance of both chromic acid and benzaldehyde was determined. The former was determined iodometrically and the latter as the 2,4-dinitrophenylhydrazone. When the reaction was carried out in air, benzaldehyde disappeared more rapidly than expected on the basis of the above equation by a factor of 1.08. Since Waters had noted absorption of oxygen during chromic acid oxidation,[8] the reaction was carried out in an atmosphere of oxygen in a system in which the change of volume could be determined. Under these conditions, considerable oxygen was absorbed.

The reaction was then carried out in a nitrogen atmosphere. In this case the benzaldehyde disappeared less rapidly than expected from the above equation by a factor of 0.9. A small amount of gas was evolved during the reaction. Since essentially no reaction occurred between the solvent and chromic acid in the absence of the aldehyde it may be assumed that the excess chromic acid consumption was due to induced oxidation of the solvent.[9] In order to minimize this, the oxidations were carried out in the presence of excess benzaldehyde and for the most part pseudo-first-order kinetics were obtained.

The order of the reaction with respect to benzaldehyde concentration was determined by varying the aldehyde concentration over a twenty-fold range and observing the effect on the rate at constant chromic acid and hydrogen ion concentration. The data are given in Table I. The second-order rate constants (k_2) were found to remain constant as the aldehyde concentration was increased, indicating the reaction to be first-order with respect to the aldehyde concentration.

TABLE I

EFFECT OF ALDEHYDE CONCENTRATION ON THE RATE OF OXIDATION

$[Cr(VI)] = 0.00324$ *M*, $[HClO_4] = 0.0305$ *M*, $[NaClO_4] = 0.0200$ *M*, $T = 30.0°$

[RCHO]	$k_1 \times 10^4$, sec.$^{-1}$	$k_2 \times 10^3$, sec.
0.1937	10.0	5.16
.0974	5.15	5.29
.0649	3.17	4.88
.0486	2.36	4.86
.0486	2.31	4.75
.0325	1.64	5.05
.0292	1.48	5.06
.0163	0.79	4.87
	Av.	4.99 ± 0.15

The order with respect to hydrogen ion concentration was obtained in a similar fashion at constant chromic acid and benzaldehyde concentrations. The pseudo-first-order rate constants and the constants obtained by dividing these by the acid concentration (including a correction for the autoprotolysis of the solvent) are given in Table II. The latter constants vary from run to run, indicating that there is not a simple first-order dependence on hydrogen ion. A plot of the logarithm of the rate constants against H_0 using the values of

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[7] Corrections for ionic strength changes were made using 0.190 *M* sodium perchlorate for chromium(VI) solutions 0.004–0.008 *M*, and for 0.0158 *M* chromium(VI) a 0.164 *M* sodium perchlorate concentration was used.

[8] W. A. Waters, *J. Chem. Soc.*, 1151 (1946); *Trans. Faraday Soc.* **42**, 184 (1946).

[9] Induced oxidation, involving oxidation by chromium species of intermediate valence, has been commonly observed during chromic and oxidations (F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1948)). Apparently, the intermediate chromium species are stronger oxidizing agents than chromium(VI).

the latter reported previously,[10] gave a good correlation (Fig. 1) with a slope of 1.07.

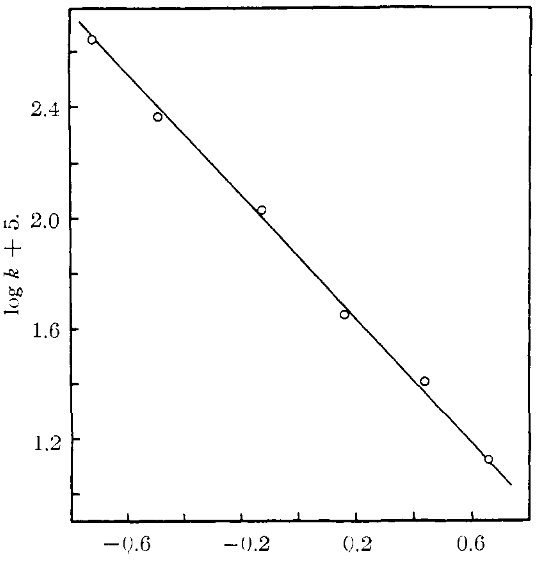

Fig. 1.—Rate of chromic acid oxidation of benzaldehyde as a function of H_0.

TABLE II

EFFECT OF ACID CONCENTRATION ON THE RATE OF OXIDATION

[Cr(VI)] = 0.00255 *M*, [RCHO] = 0.1205 *M*, ionic strength = 0.303, *T* = 30.0°

$[H^+]$, *M*	$k_1 \times 10^3$, sec.$^{-1}$	$k_1/[H^+] \times 10^3$, sec.$^{-1}/M^{-1}$
0.300	2.78	9.27
.201	1.43	7.11
.101	0.660	6.53
.101	.657	6.50
.101	.666	6.59
.0296	.158	5.34
.0177	.086	4.86

The effect of chromium(VI) concentration on the rate also was determined. Good first-order rate plots were obtained with each concentration, but the slopes of the plots (Fig. 2) changed with changing concentration. The rate constants are given in Table III. This is reminiscent of the effect noted by Novick and Westheimer[11] in the study of the chromic acid oxidation of isopropyl alcohol.

TABLE III

EFFECT OF CHROMIC ACID CONCENTRATION ON THE RATE OF OXIDATION

$[HClO_4]$ = 0.100 *M*, [RCHO] = 0.100 *M*, ionic strength = 0.301, *T* = 30.0°

[Cr(VI)], *M*	$k_1 \times 10^4$, sec.$^{-1}$	k_1 (cor.) $\times 10^4$, sec.$^{-1}$
0.00145	7.56	8.2
.00261	7.18	8.1
.00523	6.03	7.5
.00523	5.92	7.4
.00787	5.22	7.3
.0142	4.57	7.1

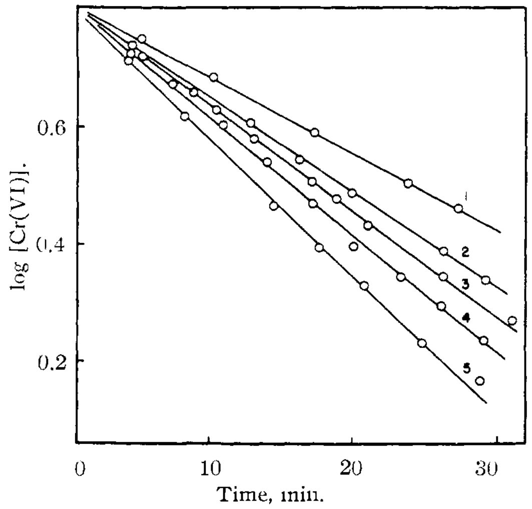

Fig. 2.—First-order plots for the chromic acid oxidation of benzaldehyde with different initial chromic acid concentrations: 1, 0.0142; 2, 0.00787; 3, 0.00523; 4, 0.00261; 5, 0.00145 *M*.

They found that the rate of reaction could, however, be correlated with the acid chromate concentration. This is not directly proportional to the chromium(VI) concentration because of the monomer–dimer equilibrium

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$

The equilibrium constant for this reaction has been determined spectrophotometrically in water solution using deviation from Beer's law of the chromium(VI) solutions.[12] It did not seem reasonable to use the same value for the constant in 91% acetic acid since the large change in dielectric constant in going from water to this solvent would favor the acid chromate form, the decrease in water content of the solvent would favor the dichromate form (the equilibrium constant as usually given does not include the concentration of water) and if ion pairs are formed in this medium it would be expected that they would have a higher ion pair association constant for the dichromate ion than for the univalent acid chromate ion and this again would favor the dichromate ion. It did not appear practical to try to assess the magnitude of these effects.

A spectrophotometric investigation of the equilibrium in 91% acetic acid was, therefore, undertaken. The data for several wave lengths and a 158-fold change in chromium concentration is shown in Fig. 3 and a curve for one wave length for an aqueous solution is included for comparison. It is immediately evident that the equilibrium constant is smaller in 91% acetic acid than in water. A comparison of the positions of the initial reflection suggests that it is less by about a factor of five (*K* = 98 for the curve shown for aqueous solution). An attempt was made to determine the equilibrium constant from these data. Since Beer's law was followed at the low concentration end, it was assumed that the extinction coefficient so determined will be that appropriate for the acid chromate ion.

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(10) K. B. Wiberg and R. J. Evans, THIS JOURNAL, **80**, 3019 (1958).

(11) A. Novick and F. H. Westheimer, *J. Chem. Phys.*, **11**, 506 (1943).

(12) J. Tong and E. King, THIS JOURNAL, **75**, 6180 (1953).

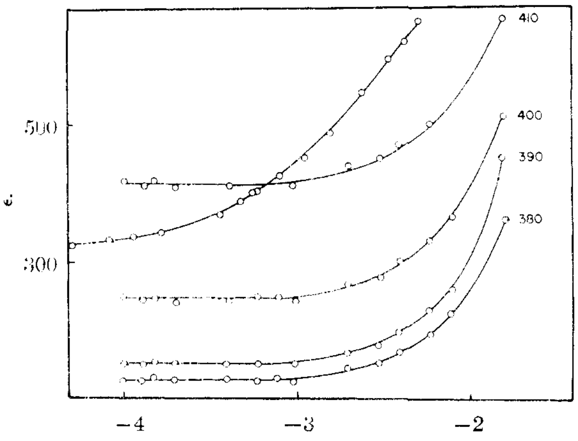

Fig. 3.—Extinction coefficient for Cr(VI) as a function of concentration.

The spectra were determined at a constant ionic strength (0.300 *M*), using an acid concentration (0.100 *M*) which was estimated to convert all of the chromate ion to the acid chromate ion but not to form any significant amount of chromic acid. Analyses were carried out using the method of King and Tong.[12] If y is a fraction of chromium(VI) in the dimeric form and c is the stoichiometric concentration of chromium(VI), then

$$2Kc = y/(1 - y)^2 \qquad (1)$$

and

$$\epsilon_{obs} = \epsilon_1 y + \epsilon_2(1 - y) \qquad (2)$$

where ϵ_{obs} is the observed extinction coefficient, ϵ_1 is that of the dimer (actually one-half the molar extinction coefficient) and ϵ_2 is that of the monomer. A value of K is assumed, the value for y calculated for each concentration and inserted into equation 2. This gives as many equations as there are solutions, although the first eight contributed nothing to the result, since at these concentrations there is only monomer. The average value of ϵ_1 obtained thereby was reinserted into equation 2 to give ϵ_t, the calculated total extinction coefficient. This was compared with the observed value as a criterion of precision. Typical data are shown in Table IV for $\lambda = 390$ mμ, $K = 25$, $\epsilon_2 = 240$, $\epsilon_1 = 600$.

TABLE IV

[Cr(VI)], *M*	ϵ_{obs} (390)	$\epsilon_2(1 - y)$	ϵ_t	$\Delta\epsilon$	Error, %
0.0020	266	220	270	− 4	1.5
.0030	273	212	282	− 9	3.2
.0040	295	205	294	− 1	0.3
.0060	328	194	311	− 17	5.3
.0080	361	184	324	− 37	11
.0158	504	158	363	−141	35

A precision was not overly satisfactory in any case and the deviation of the two highest concentrations was marked in all cases. This suggests that the equilibrium may be more complex in the present medium than in water and that a trimer or other polymer may be formed. It did not seem practical to attempt a further analysis of this equilibrium since it would be quite difficult to extend the data to higher concentrations because of the very short path lengths required, and because such an extension would require a higher precision for the measurements than appeared obtainable.

Nevertheless, the present data show the value of K for dilute solutions of chromium(VI) must lie between twenty and thirty with twenty-five as a satisfactory value. Fortunately for the present purpose it was not necessary to know the value of the constant with any greater precision since the following treatment is not too sensitive to the exact value of K. The value obtained may be compared with the value of 62 which is calculated from the data of King and Tong[12] for an aqueous solution with an ionic strength of 0.3.

The rate data were analyzed as follows: If the rate of reaction were proportional to the acid chromate concentration, then

$$d[\mathrm{Cr(VI)}]/dt = k[\mathrm{HCrO_4^-}]$$

and

$$d[\mathrm{Cr(VI)}]/[\mathrm{HCrO_4^-}] = k_1 dt$$

The concentration of acid chromate may be calculated from

$$K = \frac{[\mathrm{Cr(IV)}] - [\mathrm{HCrO_4}]}{2[\mathrm{HCrO_4^-}]^2}$$

and solving the quadratic equation for $[\mathrm{HCrO_4^-}]$ giving

$$[\mathrm{HCrO_4^-}] = \frac{(1 - 8K[\mathrm{Cr(VI)}])^{1/2} - 1}{4K}$$

Substituting in the differential equation

$$\frac{4K d[\mathrm{Cr(VI)}]}{(1 - 8K[\mathrm{Cr(VI)}])^{1/2} - 1} = k_1 dt$$

setting

$$(1 - 8K[\mathrm{Cr(IV)}])^{1/2} - 1 = Z$$

and integrating gives

$$Z + \ln Z = k_1 t + c$$

The data on the rate of reaction as a function of the chromium(VI) concentration were replotted using this equation and $K = 35$[13] giving the constants in the last column of Table III. The change in rate constant with chromium(VI) concentration was markedly reduced showing that the monomeric chromium species and not the dimer or other polymer is the active oxidizing agent. The residual downward trend in the rate constants is at least in part due to the fact that the equilibrium involves species other than the monomer and dimer. On the basis of the results which have been obtained, the rate law may be written as

$$v = k[\mathrm{RCHO}][\mathrm{HCrO_4^-}]h_0$$

The effect of the medium on the rate of reaction was also examined. The effect of solvent composition is given in Table V. A marked inhibition by water was noted. It is possible that this was caused largely by a reduction in the acidity function of the medium (the chromium(VI) concentration was low enough so that essentially all of it was in the monomeric form in all solutions). A plot of the logarithm of the rate constants against

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[13] This somewhat larger value of K than obtained in the investigation of the monomer–dimer equilibrium was used in order to give a better approximation to the true acid chromate concentration at the higher chromic acid concentrations, as shown in Fig. 3.

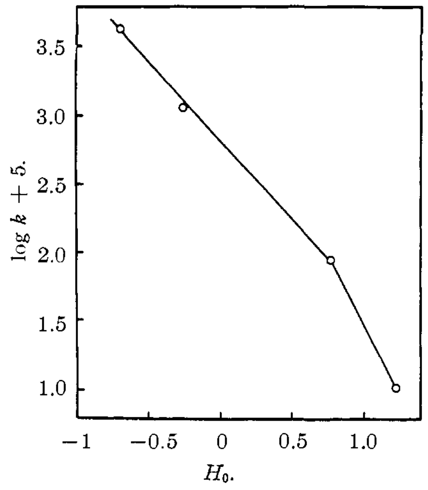


Fig. 4.—Effect of the acidity function, at constant acid concentration, on the rate of oxidation.

H_0 (Fig. 4) gave a slope of 1.1 from 75–95% acetic acid indicating that it was indeed the major effect in this range of solvent composition. In solvents containing more than 25% water, the rate of reaction decreased faster than the acidity function indicating that the effect on H_0 is not the only one which is operative.

TABLE V

SOLVENT AND SALT EFFECTS

[RCHO] = 0.253 *M*, [Cr(VI)] = 0.00505 *M*, [$HClO_4$] = 0.100 *M*

Solvent com-position	Rate constants, l. mole^{-1} sec.$^{-1}$ × 10^5 Molar ionic strength 0.306	0.256	0.156	0.106
50–50		7.66	9.56	10.8
75–25		57.8	78.8	92.7
91–9	643	703	794	1150
95–5			3280	4250

The effect of changing ionic strength was also examined giving the data in Table VI.

TABLE VI

KINETIC SALT EFFECT IN 91% ACETIC ACID

[RCHO] = 0.0235 *M*, [$HClO_4$] = 0.0471 *M*, [Cr(VI)] = 0.0157 *M*

Ionic strength	k_2	Ionic strength	k_2
0.163	0.00246	0.083	0.00362
.113	.00300	.073	.00382
.103	.00323	.063	.00418
.093	.00340		

It can be seen that the increasing ionic strength decreases the rate of the reaction. It is difficult to interpret these data since there are several effects which may cause a change in rate with changing ionic strength. For example, the acid chromate–dichromate equilibrium constant is undoubtedly a function of the ionic strength for two reasons. First, increasing ionic strength will favor the formation of a divalent ion; and secondly, a divalent ion will have a higher ion pair association constant than will a univalent ion. Both of these effects would cause the equilibrium constant to shift toward the dichromate ion as the ionic strength increases. This would correspondingly decrease the rate of reaction. It is not possible to determine from the data presently available whether this is the only effect. For this reason, all of the rate data were obtained at a constant ionic strength, and 0.300 *M* was chosen for most of the runs.

The effect of substituents on the rate of reaction was determined using benzaldehyde and seven substituted derivatives. The rate constants which were obtained are given in Table VII and a plot of the logarithm of the relative rate against the Hammett σ-values[14] (Fig. 5) gave a slope (ρ) of +1.02.

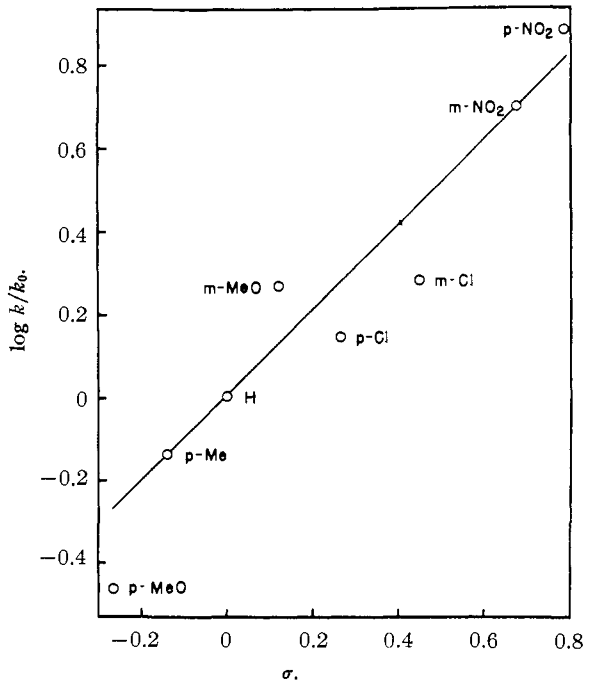


Fig. 5.—Effect of substituents on the chromic acid oxidation of benzaldehyde.

TABLE VII

EFFECT OF SUBSTITUENTS ON THE RATE OF OXIDATION

[RCHO] = 0.100 *M*, [Cr(VI)] = 0.00523 *M*, [$HClO_4$] = 0.100 *M*

Substituent	k_2, l. mole^{-1} sec.$^{-1}$ × 10^3	Rel. rate
p-MeO	1.75	0.283
p-Me	4.26	0.690
p-H	6.17	1.0
p-Cl	8.50	1.38
m-MeO	11.1	1.80
m-Cl	11.8	1.91
m-NO_2	29.6	4.79
p-NO_2	46.8	7.58

The rate of oxidation of benzaldehyde was determined at 59.94° using the concentrations which gave a second-order rate constant of 5.98 ± 0.06 × 10^{-3} at 30.01°. The rate constant was found to be 4.28 ± 0.11 × 10^{-2} indicating that the reaction has an activation energy of 13.2 ± 0.3 kcal. One may also calculate that $\Delta H^{\ddagger}$ = 12.6 kcal. and $\Delta S^{\ddagger}$ = −28 e.u. It is interesting to note that Lucchi[3] obtained an activation energy of 12.9 kcal. in approximately 75% acetic acid.

[14] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc. New York, N. Y., 1940, p. 188.

The kinetic data which have been described above is not adequate for the determination of a mechanism of the reaction since it does not give information about the order of bond making and breaking and about the structures of intermediates. One piece of information which easily may be obtained is whether or not the carbon–hydrogen bond is cleaved in the rate-determining step. This may be done by measuring the deuterium isotope effect,[15] if any. Benzaldehyde-d_1[16] was oxidized under the same conditions as used for the oxidation of ordinary benzaldehyde ($k_2 = 5.98 \pm 0.06 \times 10^{-3}$) and gave a rate constant of $1.38 \pm 0.03 \times 10^{-3}$. The isotope effect k_H/k_D is then 4.3 ± 0.1 indicating that the carbon–hydrogen bond is cleaved in the rate-determining step.

If it were possible to determine the oxidation state of the chromium species which is first formed in the oxidation (*i.e.*, chromium(V) or -(IV)), the question of whether the reaction involves a one-electron or a two-electron transfer would be answered. Watanabe and Westheimer[17] have successfully used the induced oxidation of manganous ion as a diagnostic tool in determining which chromium species is formed in the oxidation of isopropyl alcohol. For this reason the induced oxidation of manganous ion during the oxidation of benzaldehyde was investigated. The effect of manganous ion concentration on the rate of the reaction was first studied. The data are shown in Fig. 6. The upper line is based on the use of sodium perchlorate in order to maintain a constant ionic strength. Since it was possible that divalent ions behaved differently from monovalent ions in their effect on the rate of reaction, the use of magnesium perchlorate in order to maintain a constant ionic strength was explored. Although the reaction mixture containing magnesium perchlorate failed to use any oxidizing agent in the absence of benzaldehyde the rate plots were not entirely satisfactory, showing some acceleration in the beginning. An average rate constant was estimated from the data and this was used in order to establish the lower line in Fig. 6. It can be seen that a marked reduction in rate is caused by the addition of manganous ion, and if the value based on the use of magnesium perchlorate is close to being correct, then the rate of reaction is reduced to one-third of its original value.

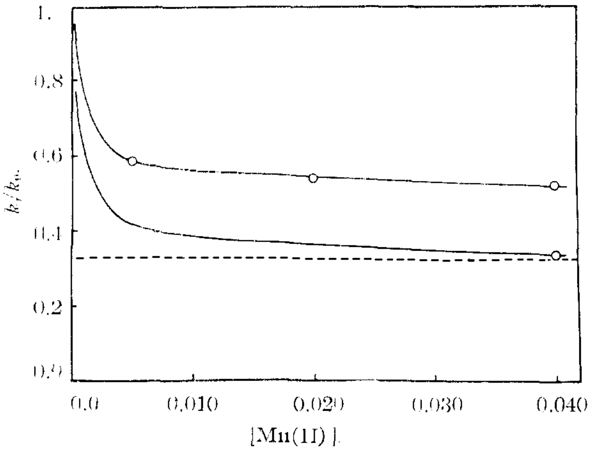
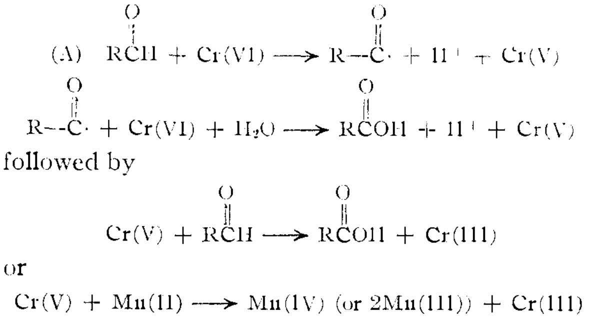


Fig. 6. Effect of Mn(II) on the rate of chromic acid oxidation of benzaldehyde.

It must be noted that the analytical procedure will determine both the chromium(VI) concentration and the concentration of the manganese species of oxidation state higher than two. An analysis of several possible schemes for the oxidation show that chromium(V) must be involved in some way. Two possible schemes which give the observed reduction in rate are



$$\text{(A)}\quad \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + \mathrm{Cr(VI)} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \mathrm{H^+} + \mathrm{Cr(V)}$$

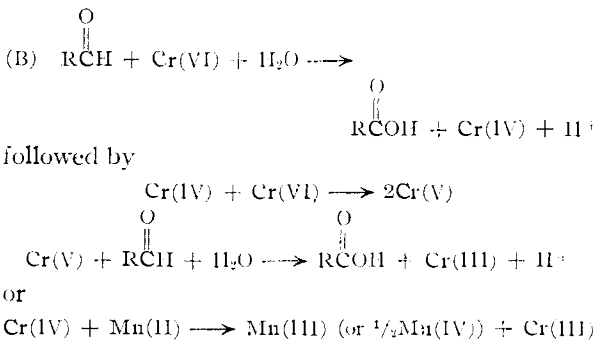
$$\mathrm{R{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \mathrm{Cr(VI)} + \mathrm{H_2O} \longrightarrow \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} + \mathrm{H^+} + \mathrm{Cr(V)}$$

followed by

$$\mathrm{Cr(V)} + \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} \longrightarrow \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} + \mathrm{Cr(III)}$$

or

$$\mathrm{Cr(V)} + \mathrm{Mn(II)} \longrightarrow \mathrm{Mn(IV)}\ (\text{or } 2\mathrm{Mn(III)}) + \mathrm{Cr(III)}$$



$$\text{(B)}\quad \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + \mathrm{Cr(VI)} + \mathrm{H_2O} \longrightarrow \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} + \mathrm{Cr(IV)} + \mathrm{H^+}$$

followed by

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)}$$

$$\mathrm{Cr(V)} + \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + \mathrm{H_2O} \longrightarrow \mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} + \mathrm{Cr(III)} + \mathrm{H^+}$$

or

$$\mathrm{Cr(IV)} + \mathrm{Mn(II)} \longrightarrow \mathrm{Mn(III)}\ (\text{or } {}^1\!/_2\mathrm{Mn(IV)}) + \mathrm{Cr(III)}$$

The reaction proceeding *via* chromium(IV) which is then oxidized by chromium(VI) to give two molecules of chromium(V) has a precedent in the work of Watanabe and Westheimer.[17] In principle, it should be possible to distinguish between the two possibilities (A and B) by determining the stoichiometry of the induced oxidation. The first scheme predicts that for each molecule of benzaldehyde oxidized there should be formed two molecules of manganese dioxide, whereas the second predicts that one molecule of manganese dioxide should be formed for each two molecules of benzaldehyde oxidized.

An attempt was made to determine the stoichiometry of the induced oxidation. It was found that the oxidized manganese species did not precipitate from the acetic acid solution. In order to obtain a standard for comparison, the oxidation of isopropyl alcohol also was examined under these conditions, and it was found that in this case also the oxidized manganese species was not precipitated during the oxidation. It seemed possible that the manganese was present as a complex acetate or other similar species. An attempt was made to use the spectrum of the solution to indicate the extent of oxidation of manganese. However, no consistent data could be obtained.

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(15) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

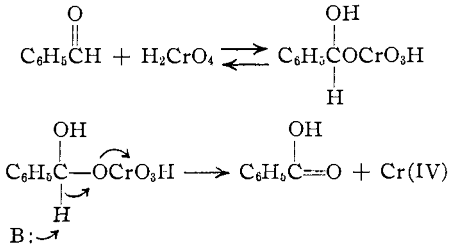
(16) K. B. Wiberg, This Journal, **76**, 5371 (1954).

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

The oxidation also was carried out in water solution in which solvent the induced oxidation of isopropyl alcohol leads to manganese dioxide which precipitates from the solution. The conditions which were suitable with isopropyl alcohol could not be duplicated because of the low solubility of benzaldehyde in water, and although a small amount of precipitate was obtained after some time this precipitate redissolved. Several attempts were made to find an analytical method which would distinguish between chromium(VI) and the higher states of manganese. No such procedure could be evolved. For this reason it is not possible at the present time to state what the stoichiometry is.

The permanganate oxidation of benzaldehyde in neutral and somewhat acidic solution proceeds at a rate which is proportional to the concentrations of the aldehyde, permanganate ion and the acid which is present. The oxidation of benzaldehyde-d_1 proceeds at one-seventh the rate of the unlabeled compound and it was found that the oxygen introduced into the aldehyde came from the permanganate using O^{18} as a tracer. These data were interpreted to indicate that the reaction proceeded *via* the formation of the permanganate ester of the hydrate of the aldehyde as an intermediate, and that this was converted to the products in the rate-determining step.[2] The similarity in rate law and isotope effect suggests that a similar mechanism may be operative in the chromic acid oxidation, and that it may be formulated as

$$HCrO_4^- + H^+ \rightleftarrows H_2CrO_4$$



$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}H + H_2CrO_4 \rightleftarrows C_6H_5\underset{H}{\overset{OH}{C}}OCrO_3H$$

$$C_6H_5\underset{\underset{B:}{H}}{\overset{OH}{C}}-OCrO_3H \longrightarrow C_6H_5\overset{OH}{C}=O + Cr(IV)$$

The last step would be rate controlling in accord with the observation of a deuterium isotope effect. It should be noted that a sequence involving the reaction of the conjugate acid of benzaldehyde with the acid chromate ion to form the above intermediate would be kinetically indistinguishable from the one written.

This type of mechanism is similar to that proposed by Westheimer[18] for the chromic acid oxidation of isopropyl alcohol, and the similarity in rate law, isotope effect and effect of manganous ion between the two chromic acid oxidations again suggests a similarity in mechanism. It is significant in this regard that Kläning[19] has demonstrated that a complex is formed between acetaldehyde and chromic acid and that it has a formation constant approximately one-half that for the complex between isopropyl alcohol and chromic acid (presumably isopropyl chromate).

The main difficulty with this mechanism is the requirement of a base in the last step. The most likely base is water but, if anything, water inhibits the reaction even beyond its effect on the acidity function. This should however be expected since the H_0 acidity function is not the correct one to use in describing the protonation of the acid chromate ion, and the H_- function should be used. The latter probably increases more rapidly with decreasing water concentration in the solvent than does H_0 since both the proton and the acid chromate ion will be hydrated, whereas the neutral product chromic acid will have a considerably lower degree of hydration. The formation constant for chromic acid will contain the h_0 function in the denominator and the concentration of water raised to some power in the numerator, and the decrease in water concentration of the medium will increase the concentration of chromic acid faster than the concentration of water required in the last step is decreased. Thus, if the H_- function had been used, catalysis by water probably would have been observed. Considering this, the mechanism appears to be in accord with the data.

Another possibility for a two-electron oxidation is the removal of a hydride ion from the aldehyde by chromic acid leaving an acylonium ion which could pick up water from the solvent to give the acid. This cannot be correct since groups such as methoxy, which release electrons, would be expected to facilitate such a reaction but are found to retard the oxidation.

The most likely one-electron process involves the abstraction of a hydrogen atom from the aldehyde by chromic acid. The acyl radical could then react with chromic acid to give the acylonium ion which would form the product. The effect of substituents makes this somewhat unlikely also, since methoxy and methyl groups usually stabilize free radicals of this type,[20] but in the present case these groups were found to retard the reaction. Thus, this type of mechanism is not favored.

One of the principal remaining problems is to determine whether this is a one- or a two-electron oxidation, and this is still being studied. The complementary data being obtained in our study of the chromic acid oxidation of diphenylmethane should also be of assistance in resolving this problem.

Acknowledgment.—We wish to thank the National Science Foundation for their support of this work.

SEATTLE, WASHINGTON

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[18] F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 64 (1951); M. Cohen and F. H. Westheimer, *ibid.*, **74**, 4387 (1952); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

[19] U. Kläning, *Acta Chem. Scand.*, **11**, 1313 (1957).

[20] C. Walling and E. A. McElhill, THIS JOURNAL, **73**, 2927 (1951); C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).