

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

The Mechanisms of Permanganate Oxidation. I. The Oxidation of Some Aromatic Aldehydes¹

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The rate of oxidation of eight aromatic aldehydes by potassium permanganate has been determined from pH 5 to 13. A general acid-catalyzed and a specific hydroxyl ion catalyzed reaction was observed. The aldehydes in which the aldehyde hydrogen had been replaced by deuterium were found to be oxidized at a much slower rate than the unlabeled compounds in neutral solution, and this deuterium isotope effect was observed to decrease with increasing pH . In neutral solution, the oxidizing agent appears to be the source of the oxygen introduced into the aldehyde, whereas in basic solution the solvent contributed a major part of this oxygen. The reaction in neutral solution probably involves the formation of a permanganate ester of the hydrate of the aldehyde, followed by a rate-determining loss of the aldehyde hydrogen as a proton. A free radical mechanism is suggested for the reaction in basic solution.

Introduction

Although potassium permanganate is one of the most important oxidizing agents in laboratory practice, the detailed mode of action in neutral and basic solution has received little study. The current availability of isotopes of hydrogen and oxygen makes it possible to investigate these reactions in a more comprehensive fashion than has been the case. The results of an investigation of the reaction between aromatic aldehydes and potassium permanganate will be reported herein.

The reaction with aldehydes has received some study. Tronov³ in 1927 determined the rate of reaction between potassium permanganate and a number of alcohols and aldehydes under a limited variety of conditions, but he did not attempt to interpret his data in terms of a mechanism. Holluta and Mutschin⁴ oxidized formaldehyde with permanganate and found the reaction to be base catalyzed. Tompkins⁵ found that the oxidation of benzaldehyde with potassium permanganate showed a linear increase of rate with increasing hydroxyl ion concentration over a very limited concentration range, and also noted catalysis by strong acids. His interpretation of these results will be considered in the Discussion section. In spite of these investigations, the detailed nature of the rate-determining step still remained obscure.

Experimental

Reagents.—In all cases, the aldehydes were purified before use. The solid aldehydes, piperonal, *p*-chloro- and *p*-nitrobenzaldehyde were recrystallized from alcohol to a constant melting point. Benzaldehyde was distilled under nitrogen immediately before use. The other liquid aldehydes, *m*-chloro-, *m*-methoxy-, *p*-methoxy- and *p*-methylbenzaldehyde, were purified through the bisulfite addition compounds and distilled before use.

Benzaldehyde-*d*₁, piperonal-*d*₁ and *p*-chlorobenzaldehyde-*d*₁ were prepared by the reduction of the properly substituted benzil with lithium aluminum deuteride⁶ followed by lead tetraacetate cleavage.⁷ In the case of piperil and di-*p*-chlorobenzil, the low solubility in ether precluded the addition of a solution of the benzil to the deuteride solution as

previously described.⁵ The benzil therefore was placed in the thimble of a Soxhlet extractor and extracted into the ether solution of the deuteride. The aldehydes were purified through the bisulfite addition compound before use. Except for the infrared spectrum, the physical properties of the aldehydes were essentially the same as those of the unlabeled aldehydes. Each of the aldehydes showed the characteristic double carbon-hydrogen stretching bands of the aromatic aldehyde group, which was shifted in the labeled compounds. Table I shows the position of these bands for the three aldehydes. In each case, the 3.6 μ bands of the unlabeled aldehyde were absent in the labeled compound, indicating high isotopic purity.

TABLE I

Substituent	Band, μ			
	Unlabeled		Labeled	
H	3.59	3.69	4.76	4.88
<i>p</i> -Cl	3.58	3.69	4.77	4.88
3,4-CH ₂ O ₂	3.68	3.77	4.83	4.94

Potassium permanganate-O¹⁸ was prepared by the exchange between normal potassium permanganate and water-O¹⁸.⁸ It was analyzed by thermally decomposing a sample under vacuum, followed by mass spectrometric analysis of the oxygen formed using the mass 32 to mass 34 ratio. The permanganate was found to have 1.14% O¹⁸.

Potassium manganate was prepared by heating potassium permanganate with potassium hydroxide solution.⁸ The excess permanganate was removed by washing with pyridine. The other compounds were of a reagent grade.

Kinetic Method.—The apparatus used for the kinetic runs consisted of a conical flask of 125-ml. capacity with openings for two electrodes (glass and calomel), a thermometer, a nitrogen delivery tube and a rapid delivery pipet with a 5-ml. capacity. It was immersed in a water thermostat whose temperature could be controlled to $\pm 0.03^\circ$. The total volume of solution for all runs was 50 ml., consisting in most cases of 10 ml. of buffer, 10 ml. of aldehyde solution, 28 ml. of boiled distilled water and 2 ml. of potassium permanganate solution and for those aldehydes with low water solubility, 38 ml. of the aldehyde solution, 10 ml. of buffer and 2 ml. of potassium permanganate solution were used. The pH of the solution was adjusted to the desired value by the addition of small amounts of concentrated sulfuric acid or small pellets of potassium hydroxide before the addition of the permanganate solution. In this way, the volume of the solution could be maintained essentially constant. At regular intervals, 5-ml. aliquots were removed and analyzed for the total oxidizing power.

The concentration of the aldehyde in the reaction mixture was usually about 0.002 *M*. The water solubilities of benzaldehyde, *p*-methoxybenzaldehyde, *m*-methoxybenzaldehyde and piperonal allowed 0.01 *M* solutions to be prepared, whereas the lower water solubility of the other aldehydes required the use of 0.0025 *M* solutions. These solutions were prepared by introducing known volumes of the freshly distilled liquid aldehydes, or known weights of the solid aldehydes into a volumetric flask which was filled immediately with boiling distilled water. It was found that the desired volume of the liquid aldehydes could be

(1) Taken from part of a thesis submitted by Ross Stewart to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

(2) Research fellow on leave from the Canadian Services College, Royal Roads, British Columbia, 1953-1954.

(3) B. V. Tronov, *J. Russ. Phys.-Chem. Soc.*, **59**, 1155 (1927).

(4) J. Holluta and A. Mutschin, *Z. physik. Chem.*, **150**, 381 (1930).

(5) F. C. Tompkins, *Trans. Faraday Soc.*, **39**, 280 (1943).

(6) Obtained from Metal Hydrides, Inc., on allocation from the Atomic Energy Commission.

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

(8) G. L. Zimmerman, Thesis, University of Chicago, 1949.

pipetted with an error of less than 1%. The water was boiled in order to remove dissolved oxygen and also to aid the solution of the more difficultly soluble aldehydes. The concentrations of the aldehydes also were determined by treating aliquots with 2,4-dinitrophenylhydrazine and weighing the precipitated phenylhydrazone.⁹ Good agreement was obtained between the two procedures.

In view of the well-known readiness of benzaldehyde to undergo air oxidation, several checks were made on old solutions. Titration of aliquots with standard base showed that less than 1% of the benzaldehyde had been oxidized to benzoic acid in three weeks. Piperonal seems completely inert to air oxidation in solution; no acid could be detected in a six-month old solution of piperonal saturated with air.

In the case in which the rate of disappearance of the aldehyde was determined, essentially the same procedure was employed, except that a larger volume of solution was prepared so that 50-ml. aliquots could be removed, using a 50-ml. hypodermic syringe.

Analytical Method.—In neutral and basic solution, permanganate undergoes a valence change from +7 to +4. The most desirable analytical method would be one which permitted the determination of the concentration of species with a valence higher than 4. Thus, aliquots of the reaction solution were added to arsenite solution, followed by back-titration with standard iodine solution. This method was used for a large number of experiments, but it was abandoned when it was discovered that irregular results were obtained when various amounts of standard permanganate were analyzed by this method. Further, it was discovered that the rate of disappearance of permanganate by this method was somewhat smaller than the rate of disappearance of benzaldehyde as determined gravimetrically with 2,4-dinitrophenylhydrazine, whereas the following method gave good agreement.

The method employed by Tompkins⁵ then was used. Five-ml. aliquots of the reaction solution were added to acidified potassium iodide solutions and the liberated iodine was titrated with standard sodium thiosulfate solution. To reduce air oxidation of the acidified iodide solutions, the acid concentration was kept low. When possible, the iodine was titrated immediately after the aliquot was removed from the reaction solution. When the permanganate-aldehyde reaction was fast, this was not possible, and the solutions were titrated in random order. In all cases, the titrations were completed within ten minutes after the liberation of the iodine. Since the thiosulfate concentration was low, 0.02 *N*, its concentration was checked frequently against both standard potassium dichromate solution and against the potassium permanganate solution used for the oxidation. The concentration of the latter solution was determined by titration with sodium oxalate.

The concentrations of the aldehydes were determined gravimetrically by precipitation of the dinitrophenylhydrazone. Tompkins⁵ determined his aldehyde concentrations by oxidation with excess standard permanganate, followed by treatment with potassium iodide and titration with sodium thiosulfate. The method was found to give somewhat uncertain results, as might be expected since Tompkins⁵ found that benzoic acid is slowly oxidized by permanganate.

Oxidations with Potassium Permanganate-O¹⁸.—A typical experiment was conducted as follows. A solution of 130 ml. of 1 *M* dipotassium hydrogen phosphate adjusted to the desired *pH* and 725 ml. of distilled water was boiled for about 15 min., or until the volume had been reduced about one-tenth. A small sample was removed and the *pH* was measured after it had cooled to room temperature. Seven hundred and fifty ml. of the boiling solution was added to a three-necked one-liter flask equipped with a stirrer, thermometer, dropping funnel and nitrogen inlet tube and set in a constant temperature bath. The flask had been flushed out with nitrogen, and a stream of nitrogen was slowly run through the apparatus during the course of the experiment. Freshly distilled benzaldehyde (1.46 ml., 0.0145 mole) was pipetted into the solution at once, and dissolved with stirring. The temperature of the bath before the addition of the hot solution was several degrees below the desired reaction temperature of 25.0°. The stirring of the solution cooled the reaction mixture quite rapidly and adjustment of

the temperature to 25.0° could be accomplished within ten minutes after the addition of the solution. Meanwhile, 1.70 g. of labeled potassium permanganate (% O¹⁸ = 1.114) was dissolved in 28 ml. of distilled water, and the reaction was begun by pipetting 25 ml. of this solution (0.0096 mole) into the reaction vessel. The reaction was quenched at the desired degree of completion by the addition of 50 ml. of 0.5 *M* sodium bisulfite. The solution was acidified with concentrated sulfuric acid until the manganese dioxide dissolved and then extracted with benzene. The benzene solution was washed with water and extracted with 40 ml. of 0.5 *M* potassium carbonate solution. This was acidified, chilled and filtered. The average yield of benzoic acid was 0.40 g.

Determination of O¹⁸ Content of the Benzoic Acid.—Dry, carbon dioxide-free nitrogen was bubbled through a capillary into a Pyrex test-tube containing 2 ml. of dry synthetic quinoline and about 50 mg. of copper powder. A side-arm on the test-tube was connected to two traps in series. The first was cooled in a Dry Ice-acetone-bath in order to remove the benzene formed. The second was fitted with small stopcocks at both ends, and could be immersed in liquid nitrogen to trap the carbon dioxide. The sample to be decarboxylated was divided into three portions of about 125 mg. each. The first was added to the copper-quinoline mixture which was then heated to reflux for five minutes. After the apparatus had been swept out for ten minutes, the second sample was added, and after the second trap had been immersed in liquid nitrogen, the solution was heated as before. The second trap was replaced by an identical trap and the procedure was repeated using the third sample. Mass spectrometric analysis of the carbon dioxide allowed a calculation of the oxygen isotope content of the benzoic acid using the following equation which is based on the normal O¹⁸ isotope content of 0.204%, and the fact that only one of the two oxygens could arise from the oxidizing agent.

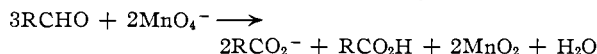
$$\% \text{ O from KMnO}_4 = \frac{2y - 0.408}{x - 0.204} \times 100$$

$$2y = \frac{I_{\text{mass}^{46}}}{I_{\text{mass}^{44}} + I_{\text{mass}^{46}}}$$

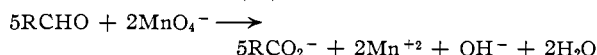
$$x = \% \text{ O}^{18} \text{ in KMnO}_4 = 1.114$$

Results and Discussion

(a) **General.**—Before determining the rate of reaction between benzaldehyde and potassium permanganate, it was necessary to determine whether or not the *pH* altered during the course of the reaction when no buffers were used. Despite Tompkins' intimation that the hydroxyl ion concentration should rise as the reaction proceeds,⁵ an examination of the stoichiometry of the reaction shows the reverse condition should prevail



The *pH* does indeed drop as the reaction proceeds, and its levels off at 4.5 if the reaction mixture were neutral at the beginning. This is the expected value since the solution should contain benzoic acid and benzoate ion in the ratio of 1:2, and the *pK_a* of benzoic acid is 4.2. A similar result was obtained with piperonal. It is worth noting that a rise in *pH* would be expected if the permanganate were reduced to Mn(II).



The change in *pH* with time made the use of buffers mandatory. Only phosphate and carbonate buffers were used in this work since permanganate reacts with all other common buffer systems except the borates in the *pH* range studied. The latter were not used because of the

(9) J. Mitchell, "Organic Analysis," Academic Press, Inc., New York, N. Y., p. 279.

APPENDIX: RATE CONSTANTS AT SELECTED pH VALUES

The temperature was 25.0° unless otherwise stated. The buffers were: P, orthophosphate; Y, pyrophosphate; C, carbonate. The latter A in the last column indicates that the rate accelerated with time; S indicates it slowed with time; and M indicates that manganate was used instead of permanganate. Aldehyde concn. was about 0.002 M. When duplicate detns. were made, the higher value of the rate constant was recorded. Estimated av. error in rate constants is 3%.

pH	Buffer	k		pH	Buffer	k	
Benzaldehyde							
5.20	P 0.20	0.475		5.20	P 0.20	0.401	
5.85	P .20	.394		7.10	P .20	.302	
6.80	P .20	.370		9.10	P .20	.320	
7.72	P .20	.370		11.16	P .20	.570	
9.35	P .20	.367		11.9	P .20	.772	
11.06	P .20	.480		12.6	P .20	1.24	
12.43	P .20	.733		6.50	P .02	0.278	
13.0	P .20	.865		6.50	P .02	.472	T = 34.9°
5.20	P .02	.460	$\mu = 1.9$	6.50	P .02	.860	T = 44.9°
5.20	P .04	.482	$\mu = 1.9$	7.20	C .20	.55	
5.20	P .20	.540	$\mu = 1.9$		KOH .01	.86	$\mu = 0.125$
5.20	P .38	.581	$\mu = 1.9$		KOH .025	1.32	$\mu = .125$
5.20	P .56	.650	$\mu = 1.9$		KOH .05	1.80	$\mu = .125$
5.20	P .56	.620	$\mu = 1.9$		KOH .10	2.32	$\mu = .125$
5.20	P .72	.683	$\mu = 1.9$	12.6	P .20	1.65	M
5.20	P .76	.700	$\mu = 1.9$	<i>m</i> -Chlorobenzaldehyde			
6.50	P .02	.324		5.20	P 0.20	0.380	
6.50	P .02	.431	T = 30.0°	9.25	P .20	.290	
6.50	P .02	.795	T = 40.0°	11.46	P .20	1.00	
6.50	P .02	1.02	T = 45.0°	12.3	P .20	1.98	
5.20	Y .20	0.662		6.50	P .02	0.258	
6.65	Y .20	.630		7.20	C .20	0.442	
7.20	Y .20	.561			KOH .01	1.32	$\mu = 0.125$
8.10	Y .20	.440			KOH .025	2.08	$\mu = .125$
5.96	C .20	.605			KOH .05	3.23	$\mu = .125$
6.88	C .20	.643			KOH .10	4.60	$\mu = .125$
7.45	C .20	.588		12.6	P .20	1.25	M
8.00	C .20	.502		<i>p</i> -Nitrobenzaldehyde			
8.40	C .20	.465		5.23	P 0.20	0.348	
9.60	C .20	.390		7.30	P .20	.288	
12.3	C .20	.672		9.00	P .20	.425	
	KOH .01	.568	$\mu = 0.125$	10.9	P .20	2.93	
	KOH .025	.678	$\mu = .125$	11.9	P .20	12.0	
	KOH .05	.840	$\mu = .125$	12.4	P .20	18.0	
	KOH .125	1.11	$\mu = .125$	6.50	P .02	0.224	
	.125	1.35	T = 29.0°	6.50	P .02	.440	T = 35.0°
	.125	1.60	T = 33.0°	6.50	P .02	.790	T = 44.9°
	.125	1.82	T = 37.0°	7.30	C .20	.388	
	.125	2.09	T = 41.0°		KOH .01	15.9	$\mu = 0.125$
12.64	P .20	0.89	M		KOH .02	25.4	$\mu = .125$
					KOH .03	31.5	$\mu = .125$
					P .20	19.0	M
<i>p</i> -Methoxybenzaldehyde							
5.20	P 0.20	0.60	A	12.6			
7.04	P .20	.451		<i>p</i> -Methylbenzaldehyde			
9.40	P .20	.404		5.20	P 0.20	0.552	
10.85	P .20	.376		7.70	P .20	.360	
12.10	P .20	.33	S	9.45	P .20	.386	
6.50	P .02	.385		11.5	P .20	.487	
6.50	P .02	.640	T = 35.0°	12.4	P .20	.502	
6.50	P .02	1.20	T = 45.0°	6.50	P .02	.341	
7.40	C .20	0.70		7.00	C .20	.77	
	KOH .125		S		KOH .05	.42	
12.6	P .20	.20	M	12.6	P .20	.450	M
<i>m</i> -Methoxybenzaldehyde							
5.25	P 0.20	0.80	A	5.4	P 0.20	0.52	A
9.25	P .20	.347		7.20	P .20	.420	
11.35	P .20	.680		9.00	P .20	.362	
12.80	P .20	1.34		10.9	P .20	.383	
6.50	P .02	0.316		12.8	P .20	.39	S
7.40	C .20	.97		7.55	C .20		A
12.6	P .20	1.25	M	6.50	P .02	0.345	
				12.8	P .20	.28	M

uncertainty regarding the species of acid present in their solutions. In very basic solution (pH 12) buffers may be dispensed with since the hydroxyl ion concentration is great enough to keep the pH from dropping appreciably during the reaction.

The pH range was from pH 5 to 13. If the pH were lowered much below 5, an autocatalytic reaction appeared. Tompkins⁵ had observed this in solutions containing perchloric or sulfuric acid and showed that it was dependent only on the pH . Figure 1 shows a second-order plot for the reaction between permanganate and benzaldehyde at pH 4.3 in solutions buffered with phosphate. The reaction clearly shows acceleration with time.

In all the kinetic experiments the aldehyde to permanganate ratio was 3:2. The concentration of the oxidizing species was determined iodometrically, and the rates were calculated on the basis of permanganate being the only oxidizing species besides manganese dioxide. The second-order rate constants were calculated using the equation, where

$$k_2 = \frac{1}{t[RCHO]} \times \frac{V_0 - V_t}{V_t - 2/5V_0}$$

V is the volume of thiosulfate required for the titration at zero time and at time t . In general, quite satisfactory linear plots were obtained over the whole pH range when $(V_0 - V_t)/(V_t - 2/5V_0)$ was plotted against time, indicating the second-order nature of the reaction (Fig. 1). In a few cases, the reaction showed either acceleration or retardation with time. These runs are indicated by the letters A or S, respectively, in the Appendix. In most cases, the reaction was carried to over 60% of completion.

The effect of concentration on rate was determined at pH 6.5 in dilute phosphate buffers. These conditions were chosen to minimize the general acid-catalyzed reaction (to be discussed later) and because it represents the pH at the middle of the region in which the rate of reaction is comparatively little affected by a change in pH . The results are shown in Table II, together with the result of one experiment in which the rate was followed by measuring the rate of disappearance of benzaldehyde. A drift in rate is apparent, but it is small considering the fifteen-fold change in concentration of both components.

TABLE II

RATE CONSTANTS AS A FUNCTION OF COMPONENT CONCENTRATION IN 0.02 M PHOSPHATE AT 25°; pH 6.5	
Benzaldehyde ^a	k , 1. mole ⁻¹ sec. ⁻¹
0.010	0.302
.020	.324
.020	.322
.051	.330
.076	.357
.152	.384
.152	.377 ^b

^a The permanganate concentration was in all cases $2/3$ that of the aldehyde. ^b This rate was determined by following the disappearance of benzaldehyde.

To determine the value of V_∞ and to see whether or not it agreed with the theoretical value of $2/5V_0$, 5-ml. aliquots were titrated at $t = 24$ hr.

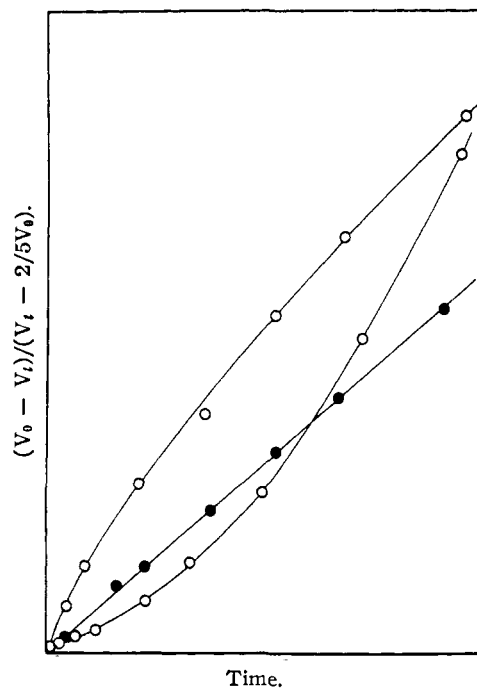


Fig. 1.—Rate plots for the permanganate oxidation of benzaldehyde at pH 4.3 (lower curve): benzaldehyde in 0.125 M potassium hydroxide (middle curve, closed circles); and p -methoxybenzaldehyde in 0.125 M potassium hydroxide (upper curve). The middle curve is typical of most of the rate plots.

for several kinetic experiments. The results are shown in Table III, where V_∞ is the volume of thiosulfate required. The agreement was good over most of the pH range, but began to deviate near pH 5.

TABLE III

VOLUME OF 0.02 N THIOSULFATE REQUIRED FOR TITRATION OF 5 ML. OF REACTION MIXTURE

Buffer	Buffer concn.	pH	k , 1. mole ⁻¹ sec. ⁻¹	V_∞ ml.	$2/5V_0$ ml.
Phosphate	0.20	13.0	0.865	0.65	0.65
Phosphate	.02	12.5	.710	.65	.66
Phosphate	.20	11.3	.487	.69	.66
Phosphate	.20	9.4	.367	.67	.65
Carbonate	.20	8.0	.500	.66	.65
Phosphate	.20	7.7	.370	.66	.65
Phosphate	.20	5.9	.394	.65	.65
Phosphate	.02	5.2	.460	.55	.65
Phosphate	.06	5.2	.507	.53	.65
Phosphate	.38	5.2	.580	.53	.65
Phosphate	.56	5.2	.650	.54	.65
Phosphate	.72	5.2	.683	.54	.65
No buffer60	.65
Phosphate	.20	4.348	.65

The experimental values of V_∞ which are less than the theoretical value of $2/5V_0$ can be accounted for either by the decomposition of manganese dioxide into oxygen and manganese of a lower valence state, or by slow oxidation of benzoic acid by manganese dioxide. It should be mentioned that the phosphate buffer, except in very basic solution, prevents the appearance of the

characteristic precipitate of manganese dioxide for a long period. Since the rate constants increased with an increase in the concentration of the phosphate buffer near pH 5, a fact which will be discussed in detail later, and since the disparity between V_{∞} and $2/5 V_0$ occurred near pH 5, it was important to show that the two phenomena were not connected. Since the value of V_{∞} was not affected by the change in buffer concentration, it would appear that they are not and that the low values of V_{∞} are caused by a slow decomposition of $Mn(IV)$ when this species is kept in solution, possibly as a complex phosphate, at mildly acid pH .

A great many experiments were performed to determine the effect of pH and buffer species on the rate of permanganate oxidation of benzaldehyde and substituted benzaldehydes. The results are shown in Fig. 2 for five aldehydes in 0.20 M phosphate buffer. The solutions were adjusted to the desired pH by adding either concentrated sulfuric acid or solid potassium hydroxide to 0.2 M dipotassium hydrogen phosphate solutions,

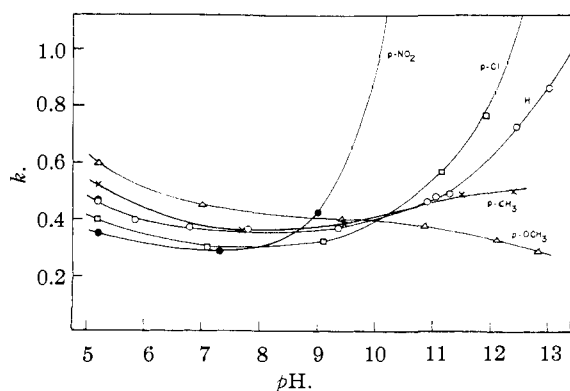


Fig. 2.—Rate constant vs. pH for substituted benzaldehydes in 0.2 M phosphate buffer.

The plots in Fig. 2 suggest that there are at least two distinct mechanisms for the permanganate oxidation of aromatic aldehydes. In the basic region, a very great difference in rate was observed for the various aldehydes. At neutral and slightly acid pH , there was a much smaller difference in rate and in the opposite direction to that observed at high pH . Figure 3 shows a plot of rate against pH for benzaldehyde using several buffers at several concentrations. The rate in the basic region seems to be primarily controlled by the pH , i.e., it exhibited specific hydroxy ion catalysis. The rate in neutral and slightly acid solutions, however, seems to be a function of the buffer and its concentration. This suggests general acid catalysis. The two catalytic effects will be discussed separately in a later section.

(b) **The Deuterium Isotope Effect.**—Since the deuterium isotope effect has been found to be of considerable value in determining whether or not a carbon-hydrogen bond is broken in the rate-determining step,¹⁰ benzaldehyde- d_1 , p -chlorobenzaldehyde- d_1 and piperonal- d_1 in which the aldehyde

(10) F. A. Loewus, F. H. Westheimer and B. Vennessland, *THIS JOURNAL*, **75**, 5018 (1953); P. D. Bartlett and F. A. Tate, *ibid.*, **75**, 91 (1953); R. P. Bell, "Acid-Base Catalysis," Oxford, 1941, p. 146.

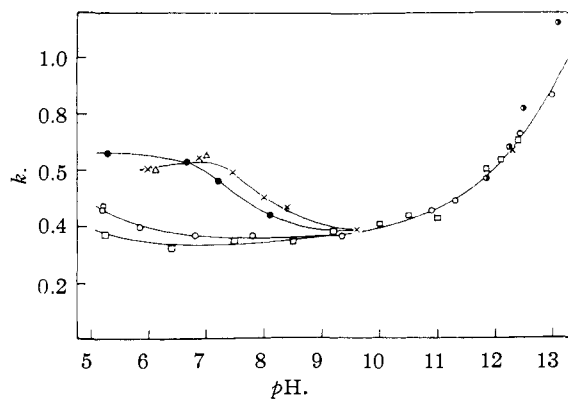
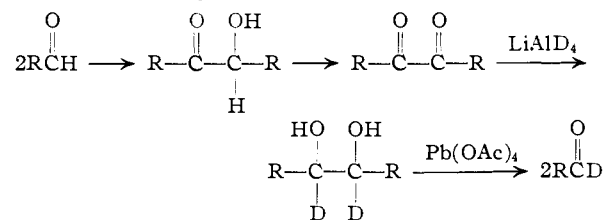


Fig. 3.—Rate constant vs. pH for benzaldehyde in various buffers: \circ , 0.2 M phosphate; \bullet , 0.2 M pyrophosphate; \times , 0.2 M carbonate; \square , 0.02 M phosphate; \ominus , potassium hydroxide; Δ , 0.1 M carbonate.

hydrogen atoms were replaced with deuterium were obtained by the route



The rate of oxidation was determined for each of these aldehydes, giving the data shown in Table IV.

TABLE IV
THE DEUTERIUM ISOTOPE EFFECT IN PHOSPHATE BUFFERS, 25°

Buffers	pH	k_D	k_H	k_H/k_D
Benzaldehyde				
0.20	5.1	0.075	0.475	6.4
.20	5.5	.060	.420	7.0
.02	6.5	.045	.323	7.2
.02	6.5	.043	.323	7.5
.20	9.4	.052	.370	7.1
.20	11.4	.170	.503	3.0
.20	12.3	.230	.680	3.0
.20	12.8	.300	.810	2.7
.20	12.7	.330	.890	2.7 ^a
p -Chlorobenzaldehyde				
0.02	6.5	0.036	0.278	7.7
.02	6.5	.037	.278	7.5
.20	7.0	.074	.550	7.4 ^b
.20	9.2	.044	.325	7.4
.20	11.9	.360	.770	2.1
.20	12.6	.660	1.24	1.9
.20	12.7	.90	1.68	1.9 ^a
Piperonal				
0.20	7.9	0.103	0.420	4.1
.20	12.7	.116	.45 ^c	3.9
.20	12.7	.090	.30	3.3 ^a

^a Potassium permanganate was replaced by potassium manganate in these experiments. ^b The phosphate buffer was replaced by carbonate in this experiment. ^c Approximate initial rate; reaction slows with time.

(c) **Oxygen Transfer.**—In order to determine the source of the oxygen introduced into the

aldehyde during the reaction, the oxidation of benzaldehyde with potassium permanganate- O^{18} was studied. The labeled permanganate was prepared by the exchange of ordinary permanganate with water- O^{18} at 100° . It has been shown¹¹ that the complete exchange of permanganate with water- O^{18} requires over 4 hours at 100° and the rate of exchange in neutral solution was found to be about 0.5% per hour at 25° . This is negligible for the present purpose. It was also shown that within wide experimental error, the rate of exchange was the same in neutral and basic solution. Benzoic acid will exchange oxygens with water only at a rather slow rate, and benzoate ion shows no appreciable exchange.¹²

The oxidations were carried out under essentially the same conditions used for the kinetic experiments, and thus the extent of reaction could be calculated from the previously determined rate constants, and the time of reaction. The benzoic acid formed was isolated and decarboxylated giving carbon dioxide which was analyzed using a mass spectrometer. The results are shown in Table V.

TABLE V
OXIDATION WITH PERMANGANATE- O^{18} IN 0.02 M PHOSPHATE BUFFER; $[MnO_4^-] = 0.0129 M$; $T = 25.0^\circ$

pH	Reaction, %	% O from MnO_4^-
Benzaldehyde		
5.5	54	75.8
5.5	90	53.9
7.2	65	67.5
9.0	65	53.6
10.6	54	31.7
12.4	54	26.4
12.4	90	17.0
Piperonal		
12.0	68	14.7

In neutral and slightly acidic solution, the oxygen in the product was derived largely from the permanganate. The amount also increased with decreasing reaction time, suggesting that the intermediate valence state of manganese (V or VI) exchanged with water before being converted to permanganate and manganese dioxide by disproportionation. The results at pH 5.5 indicate that at the beginning of the reaction, the benzoic acid was formed with essentially complete transfer of oxygen from permanganate. The extent of exchange decreased with increasing pH, and at pH 12.4, over half of the oxygen was derived from the solvent.

(d) **Thermodynamic Data.**—The enthalpies and entropies of activation were obtained at pH 6.5 in 0.02 M phosphate for the following aldehydes: benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehydes, *p*-methoxybenzaldehyde and benzaldehyde- d_1 . Rate measurements were made at least three temperatures with at least five measurements being made. Good straight line relationships were obtained when $\log k/t$ was plotted against $1/T$. Values of ΔH^\ddagger and ΔS^\ddagger were ob-

tained from the slope determined by the method of least squares.

TABLE VI
THERMODYNAMIC DATA FOR REACTION OF BENZALDEHYDE WITH PERMANGANATE; 25° , pH 6.5 in 0.02 M PHOSPHATE

Aldehyde	ΔH^\ddagger , kcal.	ΔS^\ddagger , e.u.
<i>p</i> -Methoxybenzaldehyde	10.0 ± 0.3	-26.8 ± 1
Benzaldehyde	10.3	-26.2
<i>p</i> -Chlorobenzaldehyde	10.2	-26.7
<i>p</i> -Nitrobenzaldehyde	11.1	-24.3
Benzaldehyde- d_1	11.2	-27.1

Reaction rates also were determined for benzaldehyde in 0.125 N KOH at several temperatures, but the plot of $\log k/T$ showed a curve. The enthalpy of activation was approximately 6.5 kcal. at 30° , and if the water-catalyzed reaction was still operative at this pH, this corresponds to an enthalpy of about 4.5 kcal. for the hydroxyl ion-catalyzed reaction.

(e) **General Acid Catalysis.**—Although the reaction rate varied with buffer concentration, it is obvious from Figs. 2 and 3 that an "uncatalyzed" or "neutral" reaction is operative. This rate could be due to catalysis by the general acid, water. The Hammett¹³ plot of $\log k$ against σ for this reaction is shown in Fig. 4. It was obtained at pH 6.5 using a low buffer concentration, 0.02 M phosphate. Under these conditions, the acid-catalyzed reaction contributes very little to the rate of reaction, and the base-catalyzed reaction is of no importance in any case except that of *p*-nitrobenzaldehyde. Here, a small correction should be made, and the corrected point is indi-

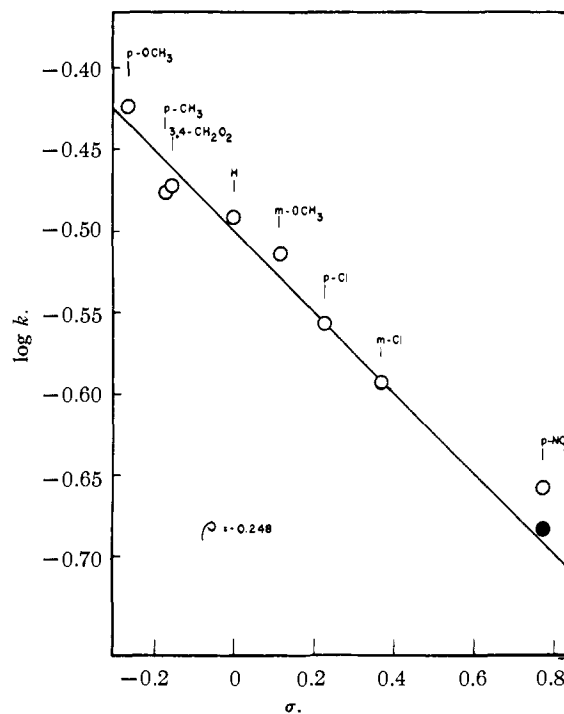


Fig. 4.—Hammett plot for benzaldehydes, pH 6.5, 0.02 M phosphate buffer.

(11) G. Zimmerman, ref. 8; G. A. Mills, THIS JOURNAL, **62**, 2833 (1940); N. F. Hall and O. R. Alexander, *ibid.*, **62**, 3455 (1940).

(12) I. Roberts and H. C. Urey, *ibid.*, **60**, 2391 (1938).

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 183-194.

cated by the solid circle. The slope is -0.248 , calculated by the method of least squares, a value similar to that obtained in most reactions which are considered to be acid catalyzed.¹³ The fact that the same relative rates were obtained in reactions catalyzed by phosphate and by carbonate (excluding piperonal and *p*-methoxybenzaldehyde which will be discussed later), indicates that the mechanism in these cases may be the same as that for the water-catalyzed reaction.

To demonstrate that general acid catalysis does occur, rates were determined in solutions containing varying amounts of buffer at constant ionic strength and *pH*, and hence containing varying amounts of undissociated acid. Since potassium pyrophosphate buffers exhibited strong catalysis, this system was studied first. The results (Fig. 5) indicate a marked catalytic effect, but the scatter of points is hardly satisfactory. The lack of precision was at first thought to be due to the conversion in solution of pyrophosphate to the poorer catalytic species, orthophosphate ion. However, this hydrolysis is believed to occur very slowly at room temperature.¹⁴ Another series of experiments were then performed with potassium orthophosphate at the same *pH*. Fortunately, the greater solubility of this salt allowed solutions of sufficient concentration to be used to obtain large catalytic effects. The data (Fig. 5) are much more precise and again indicate general acid catalysis. It might be mentioned that much larger catalytic effects were obtained when the phosphate buffers were made up from some samples of anhydrous dipotassium hydrogen phosphate. It is believed that another catalytic species, possibly pyrophosphate, was present in the samples which were available.

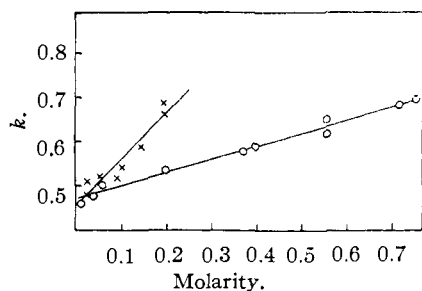


Fig. 5.—Rate constant vs. buffer concentration for benzaldehyde permanganate reaction, *pH* 5.2, in phosphate (circles, μ 1.9) and pyrophosphate (crosses, μ 1.2) buffers.

An increase in ionic strength caused only a small increase in the rate of the water-catalyzed reaction as is shown in Table VII. This effect cannot cause the increase in rate observed in going to lower *pH* in phosphate buffer, since there is actually a small decrease in ionic strength on addition of sulfuric acid to dipotassium hydrogen phosphate. It was noted that piperonal, and to a much smaller extent *m*- and *p*-methoxybenzaldehyde, reacted much faster than would be expected from consideration of the Hammett substituent constants for the methoxy and methylenedioxy groups. In addition,

(14) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1951, p. 232.

TABLE VII

EFFECT OF CHANGE IN IONIC STRENGTH ON RATE OF PERMANGANATE-BENZALDEHYDE REACTION; *pH* 6.5, BUFFER = 0.02 M PHOSPHATE

Na_2SO_4 , M	μ	k , l. mole ⁻¹ sec. ⁻¹
..	0.03	0.324
..	.03	.322
0.20	.62	.355
0.56	1.70	.372

the reaction rate accelerated with time. The acceleration was due, no doubt, in part to the fact that V_∞ (24 hr.) was smaller than $2/5V_0$. However, the shape of the curves was not changed appreciably if V_∞ was used rather than $2/5V_0$ in the calculation. Furthermore, the difference between V_∞ and $2/5V_0$ was not a function of the rate.

It appeared that the ether groups might be undergoing an acid-catalyzed reaction with permanganate, even though these aldehydes fitted quite satisfactorily on the Hammett plot for the water-catalyzed reaction. Piperonylic acid, the product of the permanganate oxidation of piperonal, was substituted for piperonal in several kinetic experiments and it was found to undergo rapid oxidation, presumably at the dioxolane function, in a carbonate buffer below *pH* 7 and in a phosphate buffer below *pH* 6. It was oxidized much more slowly in basic solution. This is possibly surprising in view of the well known stability of dioxolanes. However, it is reported that the preparation of piperonylic acid from piperonal by permanganate oxidation¹⁵ results in a low yield if the permanganate is added to the piperonal. This indicates that oxidation can occur at the ether function. *p*-Methoxybenzoic acid, on the other hand, was oxidized rather slowly by permanganate under the conditions of acid catalysis, and the small acceleration during the oxidation of the corresponding aldehyde may be due to other factors. For example, an acid-catalyzed reaction between MnO_2 and the aldehyde may occur since the aldehydes having ether groups are much more basic than benzaldehyde.

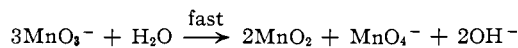
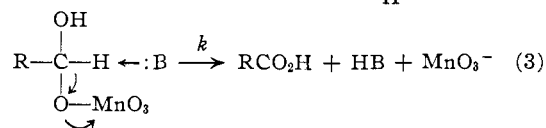
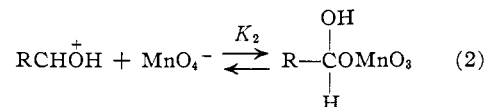
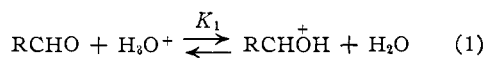
The principal observations concerning the neutral and acid-catalyzed reactions may be summarized as:

1. The rate of reaction was found to be proportional to the first powers of the permanganate and the aldehyde concentrations. The reaction was also general acid catalyzed.
2. The rate-controlling step involved the cleavage of the aldehyde carbon-hydrogen bond, as indicated by the deuterium isotope effect.
3. The oxygen introduced into the aldehyde was derived mainly from the oxidizing agent, indicating that a bond was at some time formed between the aldehyde carbon and an oxygen of the oxidizing agent.

A mechanism which will accommodate the above data is¹⁶

(15) R. L. Shriner and E. C. Kleiderer, "Organic Syntheses," John Wiley and Sons, New York, N. Y., Vol. II, p. 538.

(16) This mechanism bears a formal relationship to the mechanism of the oxidation of isopropyl alcohol with chromic acid (F. Holloway, M. Cohen and F. Westheimer, THIS JOURNAL, **73**, 65 (1951) and previous papers) in that an ester intermediate is postulated. In the chromic acid oxidation, the ester is formed utilizing the oxygen of the alcohol, whereas in this case the oxygen of the oxidizing agent forms the ester bond.



The rate law may be derived for a solution containing the acids HA, H₂O and H₃O⁺, and the bases, H₂O, HO⁻ and A⁻. Let the concentration of the intermediate ester be [x], and let the ionization constant of HA be K₁ and the ion product of water be K_w.

$$v_1 = k'[x][\text{H}_2\text{O}] = k_1[x]$$

$$v_2 = k_2[x][\text{HO}^-]$$

$$v_3 = k_3[x][\text{A}^-]$$

$$V = v_1 + v_2 + v_3$$

from 1

$$[\text{RCH}\overset{+}{\text{O}}\text{H}] = K_1[\text{RCHO}][\text{H}_3\text{O}^+]$$

from 2

$$[x] = K_2[\text{MnO}_4^-][\text{RCH}\overset{+}{\text{O}}\text{H}]$$

$$[x] = K_1K_2[\text{RCHO}][\text{MnO}_4^-][\text{H}_3\text{O}^+]$$

and

$$v_1 = k_1K_1K_2[\text{RCHO}][\text{MnO}_4^-][\text{H}_3\text{O}^+]$$

$$v_2 = k_2K_1K_2[\text{RCHO}][\text{MnO}_4^-][\text{HO}^-][\text{H}_3\text{O}^+]$$

$$v_3 = k_3K_1K_2[\text{RCHO}][\text{MnO}_4^-][\text{A}^-][\text{H}_3\text{O}^+]$$

$$V = K_1K_2[\text{RCHO}][\text{MnO}_4^-] \{ k_1[\text{H}_3\text{O}^+] + k_2K_w + k_3K_1[\text{HA}] \}$$

The first term represents catalysis by hydrogen ion. This has not been definitely observed, although it may be appearing near pH 5. Unfortunately, the reaction becomes autocatalytic in the region in which hydrogen ion catalysis would be expected. The second term represents the "neutral" reaction which was observed. The last term represents catalysis by the general acid. The data in Fig. 3 indicates that the rate of reaction is indeed proportional to the concentration of the general acid and the curves in Fig. 4 are also in agreement with this conclusion. With the pyrophosphate buffer, the rate of reaction began to increase at about pH 9, which corresponds to the initial formation of the ion HP₂O₇⁻³ according to a potentiometric titration of sodium pyrophosphate with acid. The rate continued to rise as the HP₂O₇⁻³ concentration, and later the H₂P₂O₇⁻² concentration increased. The plateau after pH 6 corresponds to almost complete conversion to H₂P₂O₇⁻². With the orthophosphate buffer, the rate began to increase at about pH 6, corresponding to the initial formation of H₃PO₄.

In the carbonate buffer, the increase in rate is limited by the solubility of carbon dioxide in water. Thus, the catalytic effect of this buffer leveled at about pH 7, and no appreciable difference in rate was observed between 0.20 and 0.10 M carbonate at pH 7 and below. The solubility of carbon

dioxide in water at 25° is 0.033 M, and thus for a 0.2 M carbonate buffer, the solution is saturated with carbon dioxide at pH 7.2. Difficulty was experienced in maintaining the pH at a constant value during the experiments involving carbonate buffers below pH 7, presumably because of the loss of carbon dioxide from the solution. This difficulty was overcome by bubbling a stream of carbon dioxide through the solution at a rate sufficient to maintain the pH constant during the course of the reaction.

The catalytic effect of an acid is seen to depend not only on its ionization constant, but also on the rate of abstraction of a proton from the intermediate, x, by the conjugate base, A⁻, of that acid. It is not surprising, therefore, that a direct correlation between catalytic effect and acid strength is lacking.

The increase in rate with increasing pH is due to hydroxyl ion catalysis, as will be shown in the next section. The order of the reaction with respect to hydroxyl ion has been determined, and these data indicate that the base-catalyzed reaction will have a negligible rate at a pH below 7 in all cases except that of *p*-nitrobenzaldehyde.

The value of ρ was observed to be negative. One would expect the rate-determining step to have a positive ρ since an electron-withdrawing group could facilitate the abstraction of a proton in this step. Thus, the equilibrium forming the intermediate ester probably has a negative ρ which is larger in magnitude than that for the rate-determining step. A similar situation is found in the chromic acid oxidation of alcohols.¹⁷

The postulation of Mn(V) as a product in this reaction is not without precedent. Lux¹⁸ has described the preparation of Na₅MnO₄ by the reduction of permanganate in strongly basic solution. This compound was found by Zimmerman⁸ to titrate as a Mn(V) compound. A number of workers have postulated Mn(V) as a product of the reduction of permanganate, including Tompkins,⁵ Duke¹⁹ and Miller and Rogers.²⁰

It has been observed that reactions in which a carbon-hydrogen bond is broken in the rate-determining step usually show a deuterium isotope effect between four- and ten-to-one if the hydrogen is removed as a proton. In the case in which the hydrogen is removed as an atom, the deuterium isotope effect is usually lower.²¹ The observation of an isotope effect of seven-to-one in neutral and slightly acid solution therefore is additional evidence supporting the ionic mechanism which has been proposed.

(17) H. Kwart and P. S. Francis, paper presented at the 126th Meeting, American Chemical Society, New York, N. Y., Sept., 1954; *cf.* Abst. 126th Meeting, p. 97-O.

(18) H. Lux, *Z. Naturforsch.*, **1**, 281 (1946). This compound also has been prepared by D. G. Levi, *Gazz. chim. ital.*, **79**, 630 (1949), and by B. Jezowska-Trzebiatowska, J. Nawojaska and M. Wronska, *Roczniki Chem.*, **25**, 405 (1951) (*C. A.*, **47**, 12073 (1953)).

(19) F. R. Duke, *J. Phys. Chem.*, **56**, 882 (1952).

(20) H. H. Miller and L. B. Rogers, *Science*, **109**, 61 (1949).

(21) *Cf.* P. D. Bartlett and F. A. Tate, *THIS JOURNAL*, **75**, 91 (1953). This is, however, not always the case since the Cannizzaro reaction (presumably ionic) has an isotope effect of 1.8 (K. B. Wiberg, *ibid.*, **76**, 5371 (1954)), and values as high as 9 have been found in free radical reactions (H. C. Urry, Abst. 12th National Organic Symposium, Denver, Colorado, June 13, 1953).

(f) **Hydroxyl Ion Catalysis.**—It has been shown that the reaction was second order at a constant pH , and that the rate increased with increasing pH . It was then necessary to determine the order of the reaction with respect to hydroxyl ion. It was obviously not first order (Fig. 4) since the rate would then be increased tenfold for each pH unit increase. Actually, about a threefold increase was noted.

The rate of reaction was determined for four aldehydes in solutions containing various amounts of potassium hydroxide at constant ionic strength. A plot of the rate constants against the square root of the hydroxyl ion concentration is shown in Fig. 6. A linear relationship was obtained in each case, indicating one-half power dependence on hydroxyl ion concentration. The intercept at the origin is the rate of the uncatalyzed or "neutral" reaction.

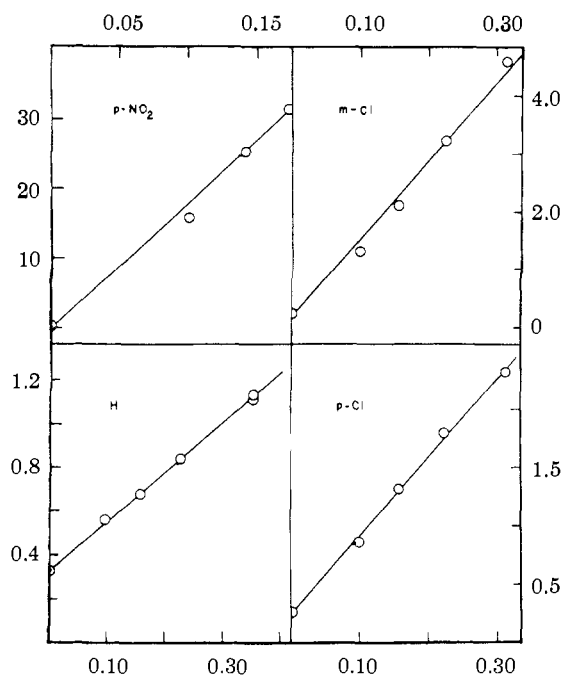


Fig. 6.—Rate constant (ordinate) vs. square root of hydroxyl ion concentration (abscissa) for four benzaldehydes.

The effect of ionic strength was found to be small, since essentially the same rate was obtained in 0.2 and 0.02 M phosphate buffers. The rate constants were found to be affected only slightly by changing the component concentration as shown in Table VIII.

TABLE VIII

RATE CONSTANTS FOR BENZALDEHYDE-PERMANGANATE REACTION AS A FUNCTION OF COMPONENT CONCENTRATION IN 0.125 M KOH AT 25°

Benzaldehyde, M	k , l. mole ⁻¹ sec. ⁻¹
0.001	1.15
.002	1.13
.003	1.11
.005	1.02
.005	1.03

The change in color of the solutions as the reaction proceeded indicated that manganate was

formed as an intermediate in the oxidation. The rate of oxidation by manganate then was determined at pH 12.6 by use of the equation

$$k = \frac{1}{[RCHO]_t} \times \frac{V_0 - V_t}{V_t - 1/2V_0}$$

The value of pH was chosen so that manganate would be stable with respect to conversion to permanganate. A Hammett¹³ plot of the data thus obtained is shown in Figure 7,²² and the rate of oxidation by permanganate under the same conditions also is shown for comparison. It is apparent that the rate of oxidation by permanganate and by manganate was essentially the same under these conditions. The slope of the line (ρ) is -1.83 , both larger and of the opposite sign to that of the neutral and acid-catalyzed reactions.

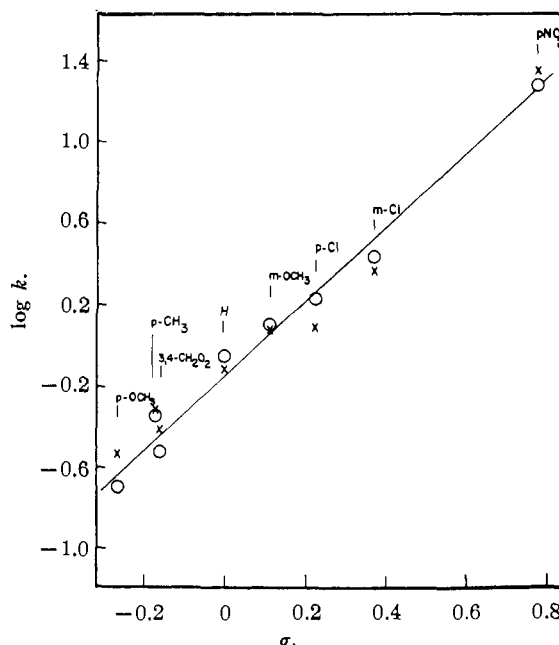


Fig. 7.—Hammett plot for benzaldehyde reacting with manganate (open circles) and permanganate (crosses) at pH 12.6, 0.2 M phosphate buffer.

The deuterium isotope effect was found to decrease with increasing pH . If one assumes that the neutral reaction is operative in basic solution, then it would appear that the isotope effect becomes very small, or perhaps disappears in this medium. For example, the rate of oxidation of benzaldehyde at pH 12.4 is about twice the neutral rate, and the isotope effect has dropped to somewhat under one-half the value at pH 6.5. Similarly, in the case of p -chlorobenzaldehyde, the rate at pH 12.6 is about four times the neutral rate, and the isotope effect is about one-fourth that observed in neutral solution. The low or non-existent isotope effect suggests that either the reaction proceeds *via* a free radical mechanism for which one might expect a low isotope effect,²¹

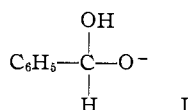
(22) The uncatalyzed reaction probably occurs under these conditions for permanganate, and there may be a corresponding reaction for manganate. However, in the absence of evidence concerning this, the uncorrected rate constants have been plotted. The uncatalyzed reaction would have only a small effect on the slope.

or that the reaction no longer involves the cleavage of the aldehyde carbon-hydrogen bond in the rate-determining step.

The transfer of oxygen from the oxidizing agent to the aldehyde was found also to decrease with increasing pH . This probably indicates that the oxygen source is now the solvent.²³ It may be noted that if the neutral reaction is operative at this pH , no oxygen need be transferred from the permanganate to the aldehyde in the base-catalyzed reaction.

The data concerning the base-catalyzed reaction may then be summarized: 1. The rate of reaction is given by the equation: $v = k[RCHO][MnO_4^-][OH^-]^{1/2}$. 2. The deuterium isotope effect is small or negligible in basic solution. 3. Most, if not all, of the oxygen introduced into the aldehyde arises from the solvent. 4. The reaction has a large negative ρ -value in contrast to the small positive value found in neutral solution.

The original proposal of Tompkins that the ion I is formed fits some of the facts. This ion could



react with permanganate by a hydride shift and the effect of substituents on the rate would be in agreement with the stability of the ion. The following points are at variance with such a mechanism, however. First-order dependence on hydroxyl ion concentration is required, and this was not found. This reaction should be accelerated by an increase in ionic strength whereas actually little effect was noted. A rate-determining step between permanganate ion and the ion, I, should proceed faster in a medium of high ionic strength since both are anions.

Since manganate and permanganate reacted with a given aldehyde with rates of the same order of magnitude, one might expect that they operate in the same way, although this is by no means required. One would expect a hydride shift to be much slower for manganate in view of the double negative charge on the ion. This mechanism, therefore, appears to be unlikely.

The evidence which is now available suggests a free radical chain mechanism for the reaction in basic solution. It has been found that a free radical, presumably the hydroxyl radical, is present in alkaline permanganate solutions.²⁴ The half-power dependence on hydroxyl ion concentration may be explained most easily by assuming that it is converted to a hydroxyl radical in the initiation step, and that two of these radicals combine in the termination step, giving hydrogen peroxide. Fur-

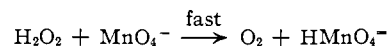
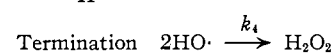
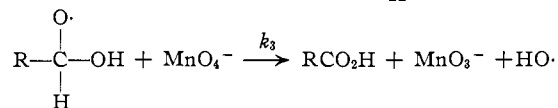
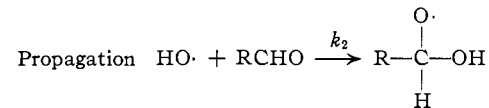
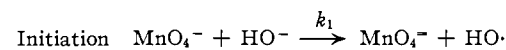
(23) The referee has suggested that permanganate may exchange oxygen with water *via* a reaction with hydroxyl radicals in the solution. It does not appear practicable to measure this experimentally, and since it is difficult to see how such a process would occur, this possibility will not be considered further.

(24) M. C. R. Symons, *J. Chem. Soc.*, 3956 (1953); *Research*, **6**, 55 (1953).

thermore, in a free radical process, one might expect the rate of reaction to be a function of the oxidation potential of the oxidizing agent. Since both permanganate and manganate have about the same potential, this might account for the similarity in rate of reaction between manganate and permanganate.

The effect of substituents is in accord with this type of reaction. Staudinger²⁵ determined the effect of substituents on the autooxidation of benzaldehyde by measuring the amount of oxygen used by the aldehyde in a given time interval. Using his data, one can estimate that *p*-methoxybenzaldehyde reacted about 0.45 times as fast as benzaldehyde, and *p*-dimethylaminobenzaldehyde reacted 0.25 times as fast. This would correspond to a ρ -value of about 1.5. In addition, it was found that *p*-chlorobenzaldehyde reacted at a faster rate than benzaldehyde.

The rate laws for a number of possible mechanisms were calculated using the steady state approximation. The requirement of first-power dependence on aldehyde concentration and half-power dependence on hydroxyl ion concentration was easily met. However, it was not possible to construct a scheme which gave first power dependence on permanganate concentration. This may be a result of the difficulty in correctly evaluating the terms with respect to the concentration of the oxidizing agent, and the fact that the possibility of reversible steps was not considered. A typical mechanism which was considered is shown below.



The rate law for this mechanism would be

$$-\frac{d[\text{MnO}_4^-]}{dt} = 3k_1[\text{MnO}_4^-][\text{HO}^-] + k[\text{RCHO}][\text{MnO}_4^-]^{1/2}[\text{HO}^-]^{1/2}$$

Since the decomposition of permanganate in basic solution is slow, the first term would be negligible with respect to the second.

It is apparent that the correct mechanism for the reaction in basic solution has not been obtained. Nevertheless, the main requirements which any mechanism must fulfill have been delineated, and evidence has been found for a free radical chain reaction.

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(25) H. Staudinger, *Ber.*, **46**, 3530 (1913).