47% overall) of the distilled ynone: bp 115–118 (2 mm); IR (neat) 2200, 1660 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (s, 9), 7.2–7.8 (m, 5); [lit.[22] bp 81–82 (1.5 mm)].

Registry No. 1, 79722-70-6; **2a**, 79722-71-7; **2c**, 79722-72-8; **2d**, 79722-73-9; **2e**, 79722-74-0; **3a**, 938-16-9; **3b**, 1009-14-9; **3c**, 2041-37-4; **3d**, 22526-24-5; **3e**, 25540-73-2; 4, 79722-75-1; **10**, 49633-73-0; 1,1,3,3-tetramethylbutyl isocyanide, 14542-93-9; *tert*-butyllithium, 594-19-4; iodobenzene, 591-50-4; *o*-bromotoluene, 95-46-5; *o*-bromoanisole, 578-57-4; 1-bromonaphthalene, 90-11-9; (*E,E*)-2,2-dimethylnon-4-en-3ylidne)amino]-2,4,4-trimethylpentane, 79722-76-2; (*E*)-1-iodo-1-hexene, 16644-98-7; (*E*)-2,2-dimethylnon-4-en-3-one, 79722-77-3; bromophenylacetylene, 932-87-6; 4,4-dimethyl-1-phenyl-1-pentyn-3-one, 32398-67-7.

Permanganate Ion Oxidations. 14. Kinetics and Mechanism of the Oxidation of Aliphatic Aldehydes in Acid Media[1,2]

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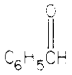
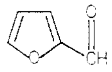
The kinetics and mechanism of the permanganate ion oxidation of 2,2-dimethylpropanal (pivalaldehyde, 4) and other aliphatic aldehydes over the pH range 2.80–6.86 have been investigated. The oxidation, which shows general-acid catalysis, is first order in [aldehyde] and first order in [MnO_4^-]. The mechanism of the Mn(VII) oxidation of aliphatic aldehydes is compared with that proposed for Cr(VI).

Although the permanganate ion oxidations[4-8] of phenylmethanal (**1**),[9-15] 2-furaldehyde (**2**),[16,17] and trifluoroethanal (**3**)[18-20] have received some study, there are no systematic mechanistic studies of the oxidation of aliphatic aldehydes.[21-26] This spectrophotometric stopped-flow kinetic study was undertaken in order to determine the mechanisms of the permanganate ion oxidation of aliphatic aldehydes in acid (eq 1)[22,23] and in neutral solution (eq 2).[10,11] It is of importance to determine whether oxidation involves general or specific acid catalysis, the free carbonyl group, and/or the aldehyde hydrate.[7,10,11,16] It is also of interest to compare and contrast the mechanisms for the permanganate ion oxidation of aliphatic aldehydes with those proposed for chromium(VI) mechanisms.[27-33]


C_6H_5CHO

1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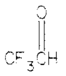
CF_3CHO

3

$$5RCHO + 2MnO_4^- + 6H^+ \rightarrow 5RCO_2H + 2Mn^{2+} + 3H_2O \quad (1)$$

In order to eliminate the possibility of enolization, we chose the oxidation of 2,2–dimethylpropanal (trimethylacetaldehyde, pivaldehyde, **4**) to 2,2-dimethylpropanoic acid (pivalic acid, **5**) for detailed study.

$$\underset{\mathbf{4}}{3(CH_3)_3CCHO} + 2MnO_4^- \rightarrow \underset{\mathbf{5}}{(CH_3)_3CCO_2H} + \underset{\mathbf{6}}{2(CH_3)_3CCO_2^-} + 2MnO_2 + H_2O \quad (2)$$

Experimental Section

Boiling and melting points are uncorrected and pH determinations were made on a Corning Digital 110 expanded scale pH meter. IR spectra were obtained on a Perkin-Elmer 283 spectrometer, and NMR spectra were obtained on a Varian EM-360 60-MHz spectrometer or a Bruker WH-90 FT NMR spectrometer.

Reagents. All solutions were prepared immediately before use. Deionized water was purified by distillation from potassium

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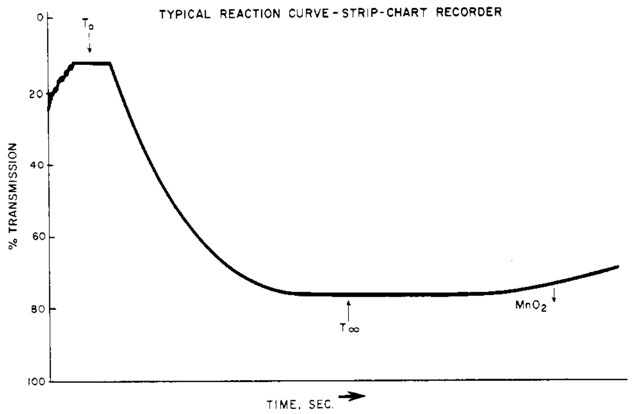

Figure 1. Typical strip-chart recorder curve where T_0 is the excess flow of reactants through the reaction cell.

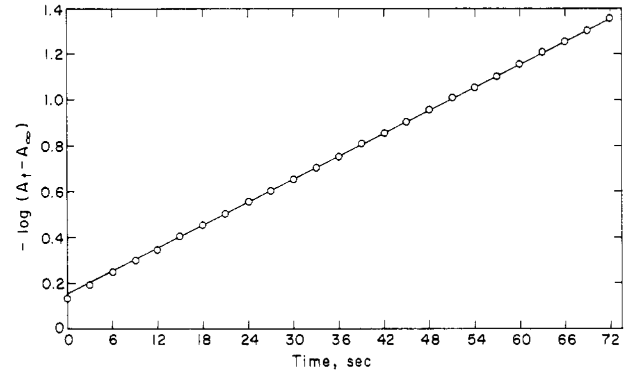

Figure 2. Typical pseudo-first-order plot of the permanganate ion oxidation of 2,2-dimethylpropanal (**4**).

permanganate in an all-glass apparatus. Reagent grade KH_2PO_4, Na_2HPO_4, HCl, and KCl were used to prepare the appropriate buffer solutions. Standard KOH or HCl solutions were added to some phosphate buffers in order to adjust the pH, and reagent grade KCl was used to maintain ionic strength. Potassium permanganate stock solutions were prepared from Acculute standard volumetric concentrates. The stock solution was stored under nitrogen in the dark, and the absorbancy index was checked before each experiment.

Propanal (**6**),[34] butanal (**7**),[35] pentanal (**8**),[36] 2-methylpropanal (**9**),[35] 2-methylbutanal (**10**),[37] 3-methylbutanal (**11**),[37] 2,2-dimethylpropanal (**4**),[34] trichloroethanal (**12**),[38] phenylmethanal (**1**),[39] and phenylethanal (**13**),[35] were fractionally distilled immediately before use.

Pivalaldehyde (**4**) was stored as the sodium bisulfite addition compound. In order to regenerate the free aldehyde (**4**) from this complex, we used the following procedure:[40] 16.0 g (0.15 mol) of Na_2CO_3 was dissolved in 100 mL of water, and the solution was placed in a separatory funnel. The bisulfite complex (19.0 g, 0.10 mol) was added to this solution, and the mixture was shaken until the complex was completely dissolved. The aqueous phase was discarded and the free aldehyde **4** was obtained in 98–99% purity with a yield of 75–80%. The aldehyde (**4**) was dissolved in diethyl ether, dried over Na_2SO_4, and filtered, and the filtrate was distilled at 77–78 °C (lit. bp 79–80 °C[41]) after careful removal of the diethyl ether.

Results

Kinetic Method. The rate of disappearance of permanganate ion was monitored spectrometrically at 510 and 524 nm in a specially designed stopped-flow reactor in a Beckman DU spectrophotometer.[42,43] The kinetics were studied under pseudo-first-order conditions, and the pseudo-first-order rate constants (k_ψ) were calculated from the slopes of the plots of $-\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ were the absorbances at 510 or 524 nm of the reaction mixture at time t and at infinity, respectively (Figures 1 and 2) by using the computer program LSKIN1.[44] All rate constants are the average of at least three experiments.

Order of Reaction. The order of reaction with respect to the concentration of **4** was obtained by measuring the rate of decrase of a constant concentration of permanganate ion at constant pH values (pH 4.20 or 6.80) in the presence of varying concentrations of **4** (Table I).[45] Plots of k_ψ (pseudo-first-order rate constant) vs. concentration of **4** gave straight lines that go through the origin at both pH values, indicating the rate of oxidation to have

Table I. Kinetic Data for the Permanganate Ion Oxidation of 2,2-Dimethylpropanal (4)[a]

pH	10^3[4], M	10^4-[MnO_4^-], M	10^2k_ψ,[b] s^{-1}	k_{obsd},[c] $M^{-1}\,s^{-1}$
4.20	2.94	4.00	1.59	5.41
4.20	4.60	4.00	2.57	5.59
4.30	5.98	4.00	3.37	5.64
4.20	8.92	4.00	5.18	5.80
4.20[d]	5.98	2.00	3.55	5.94
4.30[d]	5.98	6.00	3.37	5.64
4.20[d]	5.98	8.00	3.35	5.60
4.10	5.98	2.00	3.09	5.17
6.70	5.98	4.00	2.40	4.06
6.70	5.98	6.00	1.90	3.17
6.70	5.98	8.00	2.18	3.65
6.70	5.98	4.00	2.11	3.52
6.80	4.00	4.00	1.14	2.85
6.80	5.98	4.00	1.90	3.17
6.80	8.00	4.00	2.67	3.34
6.80	10.1	4.00	3.22	3.18
6.80	12.0	4.00	3.95	3.30

[a] Temperature 25.0 °C, $\mu = 0.30$, $\lambda = 524$ nm, KH_2PO_4–Na_2HPO_4 buffer system. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = $k_\psi/[4]$. [d] 5% KH_2PO_4 solution, $\mu = 0.30$.

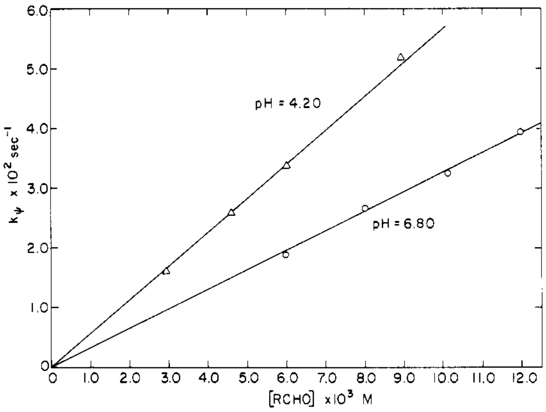

Figure 3. Effect of 2,2-dimethylpropanal (**4**) concentration on the pseudo-first-order rate constants for the permanganate ion oxidation at pH 4.20 and 6.80 at 25.0 °C.

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Table II. Effect of pH on the Permanganate Ion Oxidation of 2,2-Dimethylpropanal (4)[a]

pH	10^3[4], M	10^2k_ψ,[b] s^{-1}	k_{obsd},[c] $M^{-1}\,s^{-1}$	10(log k_{obsd}
6.7	4.00	1.18	2.95	4.60
5.6	5.98	2.34	3.91	5.92
4.6	5.98	3.12	5.22	7.18
4.3	5.98	3.37	5.64	7.51
2.8	5.98	5.14	8.60	9.34

[a] Temperature 25.0 °C, λ = 524 nm, μ = 0.3, phosphate buffers with added KOH or HCl. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = $k_\psi/[4]$.

a first-order dependence on the concentration of pivalaldehyde (4, Figure 3). At constant aldehyde (4) concentration and constant pH (pH 4.20, 6.70, 6.80), the pseudo-first-order rate constant (k_ψ) is not altered appreciably with increasing permanganate ion concentration, which indicates a first-order dependence on the concentration of permanganate ion. Figure 3 also implies a first-order dependence on [MnO_4^-].

Effect of pH. The way in which acid influences the rate of oxidation is shown in the plot of log k_{obs} against pH (Table II, Figure 4). In order to test for the occurrence of general-acid catalysis, we determined the rate of oxidation as a function of buffer concentration at constant ionic strength in order to minimize salt effects (Table III). The ratio [KH_2PO_4]/[Na_2HPO_4] was held constant in order to maintain a constant pH. Plots of the second-order rate constant (k_{obsd}) against buffer concentration (Figure 5 and 6) are linear with slopes (catalytic rate constants) of 8.50 at pH 5.9 and 5.77 at pH 5.7 and intercepts (rate constants for H_3O^+ acting as the general acid) of 3.12 and 2.40 at μ = 0.3 and 1.0, respectively.

The above kinetic data suggest that the permanganate ion oxidation of 4 in weakly acid media is overall third order (eq 3) with the possibility of some contribution from

$$\text{rate} = k_{obsd}\,[4][MnO_4^-][H_3O^+] \qquad (3)$$

the neutral reaction (eq 4 where k_0 is the observed rate constant for the neutral oxidation reaction) near pH 7.[16]

$$\text{rate} = k_0\,[4][MnO_4^-] \qquad (4)$$

Thermodynamic Parameters. The permanganate ion oxidation of 4 at 15 and 25 °C at pH 4.20 gives E_a = 9.0 kcal mol^{-1}, $\Delta H^\ddagger$ = 8.4 kcal mol^{-1}, $\Delta S^\ddagger$ = -26.6 eu, $\Delta G^\ddagger$ = 16.2 kcal mol^{-1}, and $A = 2.7 \times 10^7$ M^{-1} s^{-1}.

Substituent Effects. Table IV shows the effects of substituents on the permanganate ion oxidation of a series of aliphatic aldehydes. The aldehyde hydrate equilibrium constants[46-57] (K_{hyd}, eq 5) are also included in Table IV.

$$K_{hyd} = [>C{=}O][H_2O]/[>C(OH)_2] \qquad (5)$$

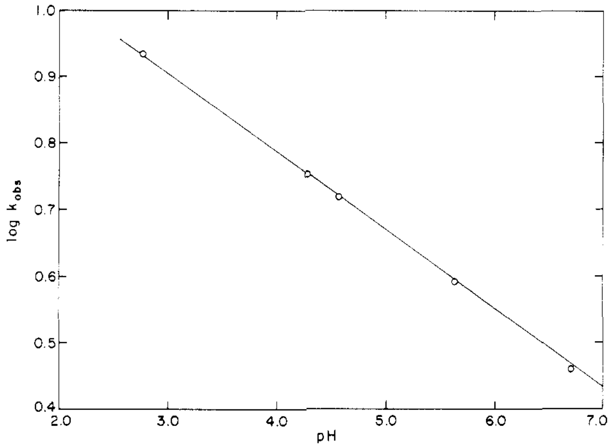


Figure 4. Effect of pH on the permanganate ion oxidation of 2,2-dimethylpropanal (4) in phosphate buffers at 25.0 °C.

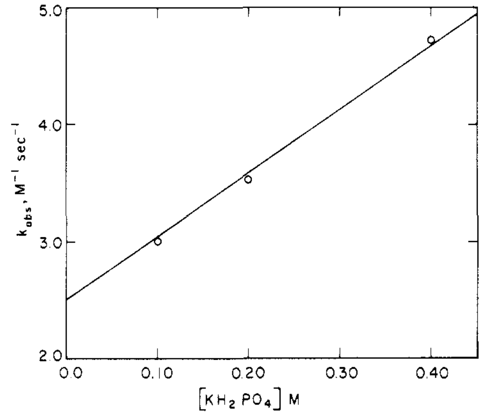


Figure 5. Rate constants vs. buffer concentrations for 2,2-dimethylpropanal (4) at pH 5.90, μ = 0.3, and 25.0 °C.

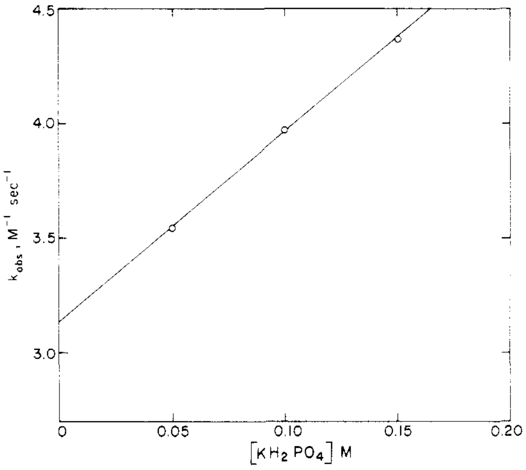


Figure 6. Rate constants vs. buffer concentrations for the permanganate ion oxidation of 2,2-dimethylpropanal (4) at pH = 5.70, μ = 1.0, and 25.0 °C.

Table III. Effects of Buffer Concentration on the Rate of Permanganate Ion Oxidation of 2,2-Dimethylpropanal (4)[a]

pH	ionic strength (μ)	[KH_2PO_4], M	[Na_2HPO_4], M	10^2k_ψ,[b] s^{-1}	k_{obsd},[c] $M^{-1}\,s^{-1}$
5.90	0.3	0.05	0.0125	2.12	3.54
5.90	0.3	0.10	0.025	2.37	3.97
5.90	0.3	0.15	0.0375	2.61	4.39
5.70	1.0	0.10	0.025	1.80	3.00[d]
5.70	1.0	0.20	0.05	2.12	3.53[d]
5.70	1.0	0.40	0.10	2.84	4.73[d]

[a] Temperature 25.0 °C, λ = 524 nm, [MnO_4^-] = 4.0×10^{-4} M, [4] = 5.98×10^{-3} M. [b] Pseudo-first order rate constant. [c] Second-order rate constant = $k_\psi/[4]$. [d] [4] = 6.00×10^{-3} M, λ = 510 nm.

Table IV. Effect of Substituents on the Permanganate Ion Oxidation of Aliphatic Aldehydes[a]

aldehyde	k_{obsd},[b] M^{-1} s^{-1} pH 4.20	k_{obsd},[b] M^{-1} s^{-1} pH 6.86	K_{hyd}[c]
C_6H_5CHO (**1**)	0.28		
$(CH_3)_3CCHO$ (**4**)	5.94	2.85	4.1
CH_3CH_2CHO (**6**)	1.35	0.78	1.4
$CH_3CH_2CH_2CHO$ (**7**)	2.07	1.12	2.1
$CH_3(CH_2)_3CHO$ (**8**)	1.92		
$(CH_3)_2CHCHO$ (**9**)	3.01	1.75	2.3
$CH_3CH_2CH(CH_3)CHO$ (**10**)	4.28	2.55	2.3[d]
$CH_3CH(CH_3)CH_2CHO$ (**11**)	2.65		
Cl_3CCHO (**12**)	very slow		3.6×10^{-5}
$C_6H_5CH_2CHO$ (**13**)	0.51		

[a] Phosphate buffers, temperature 25.0 °C, $\lambda = 524$ nm, $\mu = 0.3$. [b] Second-order rate constant = k_ψ/[RCHO]. [c] The hydration equilibrium constant.[46-57] [d] Reference 54.

The second-order rate constants (k_{obsd}) are calculated by using the total amount of aldehyde weighed for the experiment.

By use of k_{obsd} values from Table IV and E_s and σ^* values from ref 58, the following values of ρ^*, β, and h were obtained by a multiple regression analysis (eq 6):[59] at pH

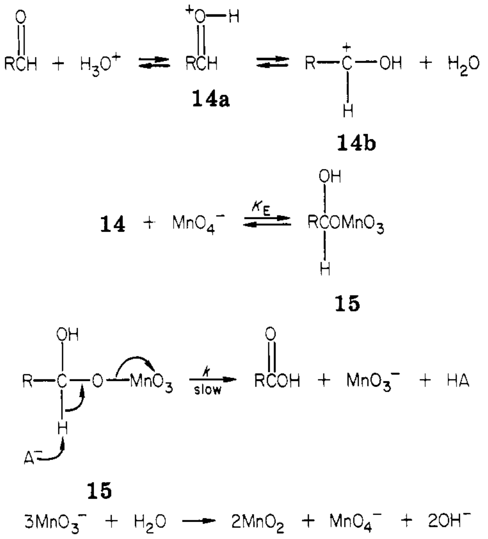
$$\log k_{obsd} = \rho^*\Sigma\sigma^* + \beta\Sigma E_s + h \qquad (6)$$

= 4.20, $\rho^* = -0.37$, $\beta = 0.37$, $h = -0.17$, r (correlation coefficient) = 0.983; at pH = 6.86, $\rho^* = -1.1$, $\beta = 0.22$, $h = -0.15$, $r = 0.945$.

Discussion

The above kinetic data are consistent with the oxidation mechanism shown in Scheme I. Although not shown in the scheme, it is recognized that the acid-catalyzed hydration of aldehydes is occurring and that the permanganate ester of the aldehyde hydrate (**15**) is in equilibrium with both the protonated aldehyde (**14**) and the hydrate. Thus, in principle, the manganese ester may arise from addition of permanganate ion to **14** or via an acid-catalyzed esterification reaction of permanganate ion with the hydrate. However, the relatively low reactivity of **12**, which is essentially 100% hydrated, suggests that permanganate ion attacks the carbonyl atom of the protonated aldehyde (**14**).

Scheme I[a]



[a] $\nu = k[\mathbf{15}][A^-]$, $\nu = kK_E[RCHO][MnO_4^-][H^+][A^-]$, and $\nu = kK_EK_{HA}[RCHO][MnO_4^-][HA]$, where K_E denotes the equilibrium constant for the formation of the permanganate ester **15** and K_{HA} is the acid dissociation constant of any acid present.

Figures 5 and 6, which show that the rates of oxidation increase linearly with increasing buffer concentration, are consistent with the general-acid-catalyzed part of the mechanism depicted in Scheme I.

Other investigators have observed primary kinetic deuterium isotope effects for the permanganate ion oxidation of **1**,[6,9] **2**,[16,17] **3**,[18] and ethanal.[22] The primary isotope effects clearly indicate that carbon–hydrogen bond breakage occurs in the rate-determining step (Scheme I). However, it is not clear whether the slow step involves hydride ion transfer or hydrogen atom abstraction. Moreover, oxygen transfer from oxidant to **1**[6,9] or to **2**[16,17] has been observed. Thus, the kinetic data in this study are in accord with previous studies of the permanganate ion oxidation of aldehydes and with chromium(VI) oxidations of aliphatic aldehydes.

Registry No. **1**, 100-52-7; **4**, 630-19-3; **6**, 123-38-6; **7**, 123-72-8; **8**, 110-62-3; **9**, 78-84-2; **10**, 96-17-3; **11**, 590-86-3; **12**, 75-87-6; **13**, 122-78-1; permanganate ion, 14333-13-2.

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