these two species react with each other to yield iodate and *o*-benzoquinone, second-order kinetics for intermediate decomposition would be observed, but this is contrary to the experimental observations. If the semiquinone reacts with the excess periodate, pseudo-first-order kinetics would be observed, but the apparent rate constant would be dependent on the periodate concentration. Again, this is contrary to the experimental observations. If the semiquinone lost an electron to the aqueous solvent, then this might correspond to the experimentally observed kinetics, but it would be highly unlikely that the solvent would act as an oxidizing agent under these conditions. More definite evidence concerning the possibility that the intermediate is a radical species should be obtained from electron spin resonance experiments now in progress.

It will not be possible to write an exact mechanism for the periodate oxidation of aromatic diols and their monoethers until further information is available concerning the structure of the intermediate involved in the oxidation of catechol. Therefore, work on this problem is proceeding along such lines.

**Acknowledgment.** The support of the National Science Foundation is gratefully acknowledged.

---

# The Kinetics of the Permanganate Oxidation of Alkenes[1]

**Kenneth B. Wiberg and Richard D. Geer**

*Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut, and The University of Washington, Seattle, Washington.* *Received May 27, 1966*

**Abstract:** The kinetics of the permanganate oxidation of alkenes was investigated at pH 6.5 and 13. The rate of the initial reaction showed a first-order dependence on the concentrations of alkene and permanganate, but was independent of the base concentration. Thus, although the products of the reaction do vary with pH, they are all probably derived from the same intermediate. Kinetic evidence was obtained for the appearance of a manganese(V) intermediate which is rapidly oxidized to a manganese(VI) species.

Bimolecular reactions characterized by rate constants in excess of 100 l. mole$^{-1}$ sec$^{-1}$ are of intrinsic interest in organic chemistry because of their relative rarity in other than proton-transfer reactions. A reaction of this type is the permanganate oxidation of alkenes. The reaction has received some previous study, particularly with regard to the products. It is known, for example, that a 1,2-diol is favored at high pH, that a ketol is favored at low pH, and that cleavage may also occur.[2,3] The diol is formed *via* a *cis* addition,[4] and the oxygen in the diol arises from the oxidant.[3] A kinetic study of the oxidation of oleate ion has been made,[5] but due to the high rates of reaction the kinetic data were not very detailed. Further, as will be shown below, oleate ion is an atypical substrate.

## Results

The alkenes used in this study were largely the salts of unsaturated carboxylic acids in order to ensure having homogeneous aqueous solutions. The reaction was studied in both neutral and basic solutions. Because of the large rate constants, the rates of reaction were determined spectrophotometrically using a stopped-flow system. Reactions with a half-life as low as 0.4 sec could be studied satisfactorily with the apparatus used.

A record from a typical kinetic run is shown in Figure 1. When the flow is started in the system, the per cent transmission decreases and levels off at a steady-state value. When the flow is stopped, the transmittance increases and approaches a constant value. Shortly thereafter, transmittance begins to decrease again as a result of the formation of colloidal manganese dioxide. The reactions were normally carried out under pseudo-first-order conditions. The rate constants were estimated from plots of $-\ln [\log (T_\infty/T)]$ against time where $T_\infty$ is the per cent transmission at a point just before colloidal manganese dioxide begins to form.

With most of the substrates investigated there was some curvature in the plots. Here, two slopes were obtained from the curves: $m_i$ represents the slope near zero time and $m_f$ represents the slope near the third half-life. An example of a curve where $m_f$ is greater than $m_i$ is shown in Figure 2a and is typical of many substrates when present in excess in alkaline solution. A case in which $m_i$ is greater than $m_f$ is shown in Figure 2b and is typical of many oxidations in neutral solution.

The reaction was found to be first order in permanganate at any pH as indicated by the data in Table I. Under the conditions used the kinetic plots were linear, and $m$ is the slope of the line. For convenience, most of the following data were obtained at a permanganate concentration of $4.0 \times 10^{-4}$ *M*.

Before considering the kinetic data in further detail we must first consider the stoichiometry of the reaction. In basic solution (above pH 12) the oxidant is reduced to manganate. The diol is the principal product, and thus a 2:1 ratio of permanganate:alkene is needed. Since the reaction is first order in permanganate, at

---

[1] This work was supported by the U. S. Atomic Energy Commission.

[2] G. King, *J. Chem. Soc.*, 1788 (1936).

[3] K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).

[4] J. Böeseken, *Rec. Trav. Chim.*, **41**, 199 (1922).

[5] S. Wolfe, Ph.D. Dissertation, University of Ottawa, 1957.

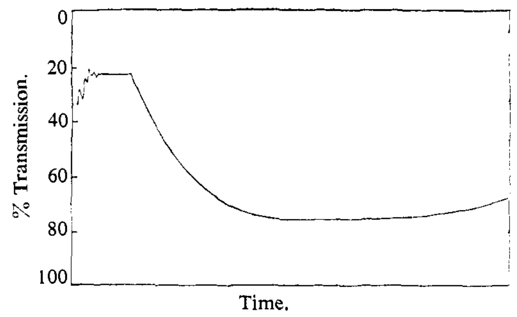

Figure 1. Typical strip chart record from a kinetic run.

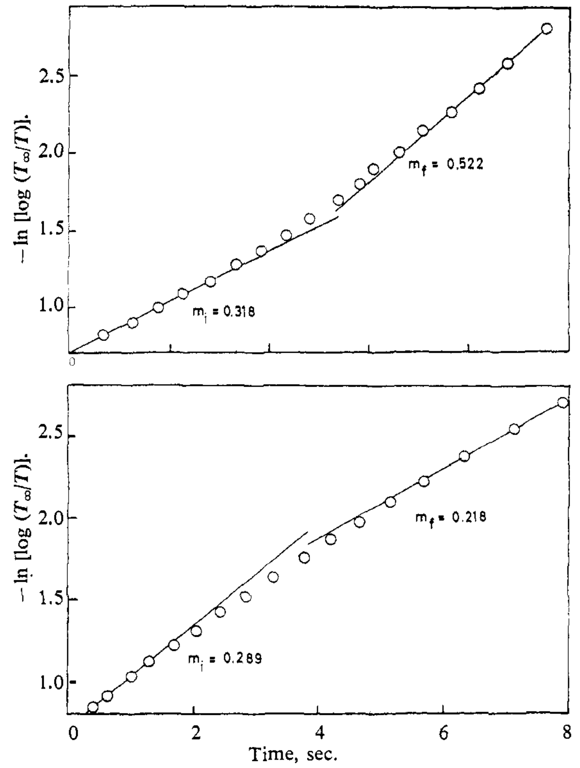

Figure 2. Typical kinetic plots for basic (upper) and neutral (lower) solutions.

least a two-step reaction sequence is required. If the first step is much faster than the second, the rate of disappearance of permanganate will correspond to the rate of the first step. However, if the reverse is true, then the observed rate will be twice that of the first step. Where the rate of the first and second step are comparable, the observed rate will fall between these limits.

Table I. Kinetic Dependence on Permanganate Concentration[a]

| [MnO$_4^-$] × 10$^4$ *M* | [Substrate] × 10$^4$ *M* | | *m* × 10$^2$ sec$^{-1}$ | Conditions |
|---|---|---|---|---|
| 4.00 | Oleate | 100.0 | 11.4 | 0.1 *M* OH$^-$ |
| 8.00 | Oleate | 100.0 | 11.4 | 0.1 *M* OH$^-$ |
| 4.00 | Crotonate | 30.0 | 113 ± 2 | 0.1 *M* OH$^-$ |
| 20.0 | Crotonate | 30.1 | 114 ± 2 | 0.1 *M* OH$^-$ |
| 4.00 | Crotonate | 30.1 | 69 ± 2 | pH 6.5 |
| 20.0 | Crotonate | 30.1 | 66 ± 2 | pH 6.5 |

[a] $T = 25.0°$; $\mu = 0.4\ M$, λ 510 mμ.

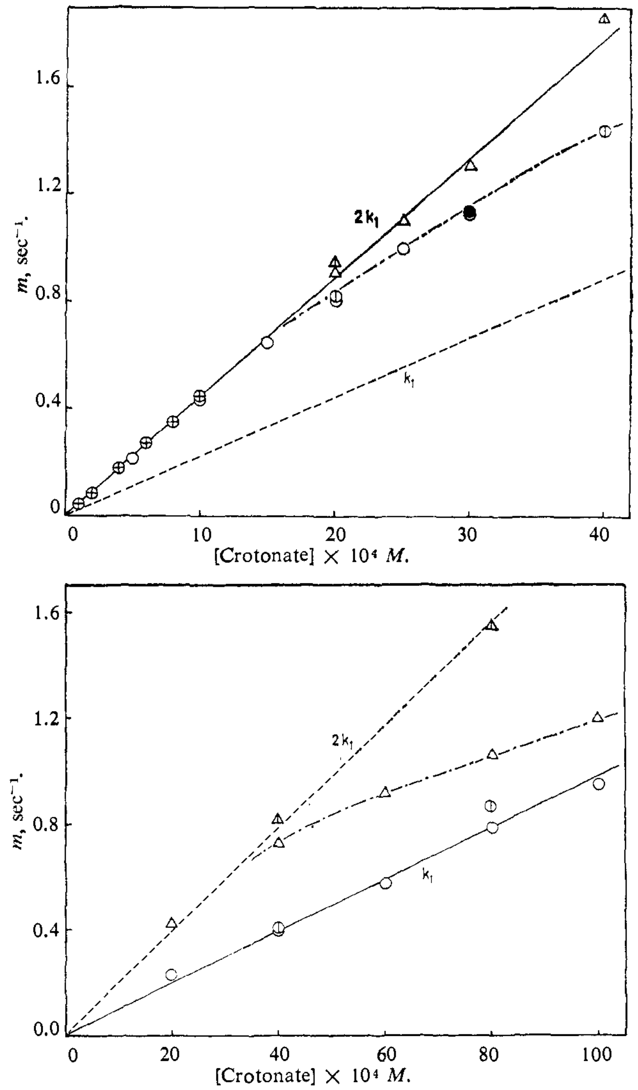

Figure 3. (a, upper) Kinetic data for the oxidation of crotonate ion under basic conditions at 25°. The data are for 510 mμ, [MnO$_4^-$] = 4.00 × 10$^{-4}$ *M*, $\mu$ = 0.4 *M*. The circles represent the $m_i$ values, the triangles represent $m_f$ values, the open symbols are for 0.1 *M* HO$^-$, the crossed symbols are for 0.05 *M* HO$^-$, the vertical lines are for 0.4 *M* HO$^-$, and the closed symbol is for 20 × 10$^{-4}$ *M* MnO$_4^-$. (b, lower) Kinetic data for the oxidation of crotonate ion under basic conditions at 0°.

The over-all reaction under neutral conditions also requires more than one step since a three-electron reduction of permanganate occurs and the oxidation products are formed by either two- or four-electron changes. Thus when ketol formation or double bond cleavage occurs the over-all reaction is

$$\text{alkene} + {}^4/_3\text{Mn}^{\text{VII}} \longrightarrow \text{ketol} + {}^4/_3\text{Mn}^{\text{IV}}$$

Therefore the observed rate may have a value from 1 to $^4/_3$ times the actual rate of the first step, again depending upon the rate and nature of the subsequent steps. If only a two-electron oxidation takes place, the reaction requires a rapid disproportionation of an intermediate manganese species to form Mn.$^{\text{IV}}$ Then the over-all stoichiometry would be

$$\text{alkene} + {}^2/_3\text{Mn}^{\text{VII}} \longrightarrow \text{diol} + {}^2/_3\text{Mn}^{\text{IV}}$$

In this case the observed rate would lie between $^2/_3$ and 1 times the actual rate of the first step.

The kinetic data for the oxidation of crotonate ion near pH 13 and at 25.0° or 0.5° are summarized in Figure 3. The data obtained at 25° and at low crotonate concentrations fall on a straight line that goes through the origin, indicating the rate of oxidation to have a first-order dependence on crotonate ion. At higher concentrations a deviation between the $m_i$ and $m_f$ values was noted. The $m_f$ values still fit on the line.

At 0.5° the difference between $m_i$ and $m_f$ is even more marked. Here the $m_i$ points lie on a straight line. The $m_f$ values give a curve which approaches the $m_i$ line at higher concentrations. Although a fourfold increase in base concentration has only a small effect on the $m_i$ values, it has a large effect on the $m_f$ values.

These data suggest that the first reaction is initially faster than the second in basic solution, but after an appreciable concentration of an intermediate has accumulated the reaction involving the second permanganate ion becomes equally fast. It is also evident that the rate of reaction involving the second permanganate ion is dependent in some way on the hydroxyl ion concentration. This interpretation assumes that the intermediate does not absorb significantly at the wavelength used in the kinetic studies. The intermediate is probably some species of manganese(V),[3] and it is known that the absorbance of manganate(V) at 510 m$\mu$ is negligible.

Based on this analysis, the initial reaction is first order in both crotonate ion and permanganate ion. At 25° the second-order rate constant ($k_1$) is 220 l. mole$^{-1}$ sec$^{-1}$, or half the slope given in Figure 3a. At 0.5°, the value of $k_1$ is obtained from the slope of the line through the $m_i$ points in Figure 3b and is 95 l. mole$^{-1}$ sec$^{-1}$.

It is also possible to estimate a rate constant ($k_2$) for the reaction of the second permanganate ion. Under pseudo-first-order conditions, the reaction of permanganate may be formalized as follows

$$\mathrm{Mn^{VII}} \xrightarrow{k_c} \mathrm{B}$$

$$\mathrm{Mn^{VII}} + \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

where $k_c = k_1[\text{substrate}]$. The rate equations

$$\frac{d[\mathrm{Mn^{VII}}]}{dt} = -k_c[\mathrm{Mn^{VII}}] - k_2[\mathrm{Mn^{VII}}][\mathrm{B}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_c[\mathrm{Mn^{VII}}] - k_2[\mathrm{Mn^{VII}}][\mathrm{B}]$$

may be solved by eliminating time as a dependent variable[6]

$$\frac{d[\mathrm{B}]}{d[\mathrm{Mn^{VII}}]} = \frac{k_2[\mathrm{B}] - k_c}{k_2[\mathrm{B}] + k_c}$$

and integrating. The observed pseudo-first-order rate coefficient ($k_o$) is given by

$$k_o = k_2[\mathrm{B}] + k_c$$

Substituting this into the integrated form of the previous expression we obtain

$$k_2 = k_c\frac{(-1 + k_o/k_c) + 2\ln(2 - k_o/k_c)}{[\mathrm{Mn^{VII}}] - [\mathrm{Mn^{VII}}]_0}$$

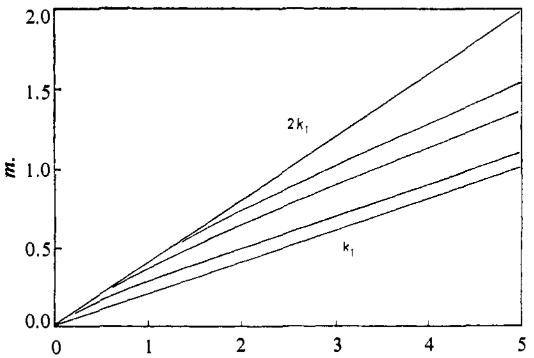

Figure 4. Theoretical slope *vs.* substrate concentration curves for a two-step reaction. The curves move toward the $2k_1$ line as $k_2$ is increased relative to $k_1$.

The value of $k_2$ could be estimated by setting $k_o$ equal to $m_f$, the slope at the third half-life. Here $[\mathrm{Mn^{VII}}]$ is $0.125[\mathrm{Mn^{VII}}]_0$. An attempt was made to obtain better values for $k_2$ by fitting the kinetic curve to calculated data obtained by numerical integration. However, the fit was fairly insensitive to the value of $k_2$; variations of ±50% could be accommodated. Thus, although a second step appears to be well established, little can be said about the details at this time. The second reaction will receive further study. The rate constants show a trend to smaller values at higher substrate concentration and are dependent on hydroxyl ion concentration. The magnitude of $k_2$ at 25° is 7-10 times that at 0.5°, which is quite different from the 2.3 ratio for $k_1$.

It is of interest to compare the curves in Figure 3 with theoretical curves based on the above treatment. The latter are shown in Figure 4. It can be seen that the theoretical curves parallel the $k_1$ line at high substrate concentration, whereas in the observed curves the points approach the $k_1$ line. It is clear that the above treatment does not take into account all the characteristics of the second reaction when calculating $k_2$. The following discussion will be concerned solely with the initial reaction characterized by $k_1$.

The oxidation of crotonate ion at pH 6.5 was studied over a sixfold range of substrate concentration at 25.0° and over a fivefold range at 0.5°. A permanganate concentration of $4 \times 10^{-4}$ *M* was used for most of the runs. The data are summarized in Figure 5. At 25.0°, except for two initial slopes at high substrate concentration the points fell on a straight line which passed through the origin. The slope was 232 l. mole$^{-1}$ sec$^{-1}$, which is in good agreement with that observed at pH 13 (220 l. mole$^{-1}$ sec$^{-1}$). This indicates that the first step in the oxidation is independent of pH. The two $m_i$ points at high substrate concentration appear to fall on a line having a slope $^4/_3k_1$, suggesting that here the second step is faster than the first, and that it leads to a four-electron oxidation of the crotonate ion.

At 0.5° the rate plots did not show curvature and a plot of the slopes ($m$) against substrate concentration gave a straight line passing through the origin. The slope was 100 l. mole$^{-1}$ sec$^{-1}$, which is very close to that observed at pH 13 (95 l. mole$^{-1}$ sec$^{-1}$). This provides further evidence that the initial oxidation step is pH independent and has a first-order dependence on substrate concentration. The data at pH 6.5 do not,

(6) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 43.

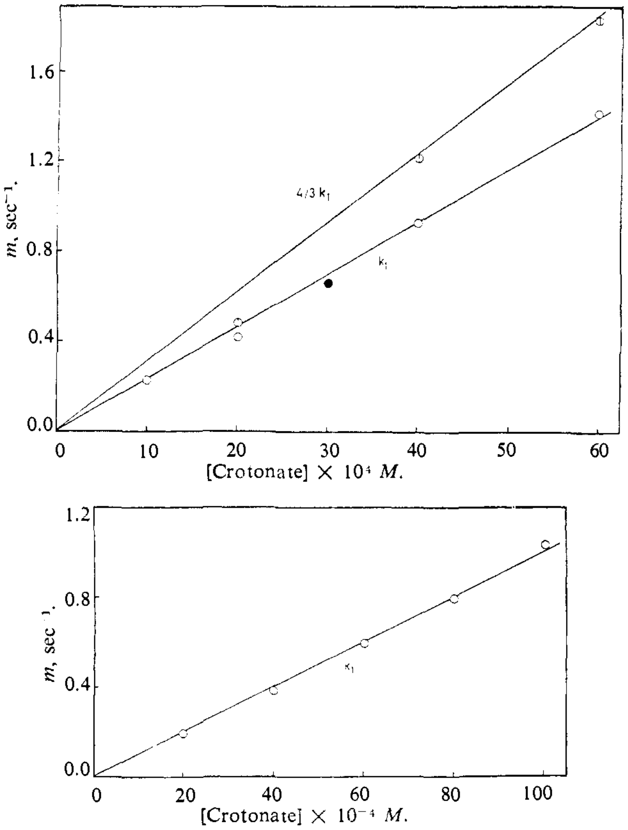

Figure 5. (a, upper) Kinetic data for the oxidation of crotonate ion at pH 6.5 and 25°. The data are for 510 m$\mu$, $[MnO_4^-] = 4.00 \times 10^{-4}$ *M*, $\mu = 0.4$ *M*. The open circles are $m_t$ values, the vertical line indicates $m_i$ values, and the closed circle is the $m_i$ value for $20 \times 10^{-4}$ *M* $MnO_4^-$. (b, lower) Kinetic data for the oxidation of crotonate ion at pH 6.5 and 0°. The data are for 510 m$\mu$, $[MnO_4^-] = 4.00 \times 10^{-4}$ *M*, $\mu = 0.4$ *M*.

however, give much information concerning the fate of the manganese-containing intermediate.

The oxidation of oleate ion has been the subject of a number of investigations.[2,5,7] This substrate is of particular interest in that it gives high product yields and a clean switch in products in going from neutral to basic solution. We have examined the kinetics of its oxidation over a 400-fold range of oleate concentration and an eightfold range of base concentrations. For most of the experiments, a permanganate concentration of $4 \times 10^{-4}$ *M* was used. The kinetic data are summarized in Figure 6. It can be seen that the reaction rate has a complex dependence on oleate concentration. At low substrate concentrations the observed rate of reaction increased rapidly with increasing substrate concentrations, but above 0.002 *M* oleate the rate of reaction increased only slowly. This behavior corresponds to micelle formation,[8] a well-known property of sodium oleate and other soaps. Above a critical concentration the size of the micelles remains about constant, but their number increases, accounting for the slow rise in rate of oxidation above 0.002 *M* oleate. At lower concentrations there is a transition to a solution of individual ions.

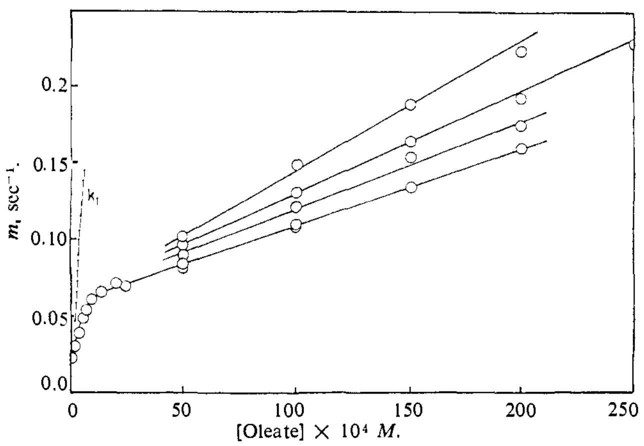

Figure 6. Oxidation of oleate ion under basic conditions. The lines in descending order are for 0.4, 0.2, 0.1, and 0.05 *M* hydroxide ion.

Because of micelle formation the use of oleate ion as a model compound does not appear satisfactory and extensions of observations based on it to other alkenes should be made with caution. It seems likely that the unusual kinetic results observed by Wolfe[5] arose from micelle formation. The product studies which gave such good yields of diol in alkaline solution (98%) were conducted at oleate concentrations well above the critical concentration for micelle formation. In a sense, the reactions were heterogeneous, making them quite different from the cases reported herein.

**Table II.** Kinetic Data for the Oxidation of Crotonate Ion, Basic Conditions[a]

| [Crotonate], $10^4$ *M* | $[OH^-]$, *M* | $m_i \times 10^2$ sec⁻¹ | $m_t \times 10^2$ sec⁻¹ | $k_2 \times 10^{-3}$ sec⁻¹ |
|---|---|---|---|---|
| | | Temperature 25.0° | | |
| 1.00 | 0.05 | 4.8 | | |
| 2.00 | 0.05 | 8.8 | | |
| 4.00 | 0.05 | 18.0 | | |
| 5.00 | 0.10 | 21.7 | | |
| 6.00 | 0.05 | 27.2 | | |
| 8.00 | 0.05 | 34.9 | | |
| 10.00 | 0.05 | 44.7 | | |
| 10.00 | 0.10 | 43.3 | | |
| 15.0 | 0.10 | 65 ± 1 | | |
| 20.0 | 0.10 | 82 ± 1 | 91 ± 2 | 23 |
| 20.1 | 0.40 | 81 ± 1 | 95 ± 3 | |
| 25.0 | 0.10 | 100 ± 1 | 110 ± 1 | 20 |
| 30.0 | 0.10 | 113 ± 2 | 131 ± 1 | 14 |
| 30.1[b] | 0.10 | 114 ± 2 | | |
| 40.2 | 0.40 | 144 ± 3 | 188 ± 1 | 12 |
| | | Temperature 0.5° | | |
| 20.1 | 0.10 | 23 ± 1 | 42 | |
| 40.1 | 0.10 | 39 ± 2 | 72 ± 1 | 3.1 |
| 40.2 | 0.40 | 40 ± 3 | 81 ± 2 | 3.5 |
| 60.2 | 0.10 | 57 ± 1 | 91 ± 2 | 2.0 |
| 80.2 | 0.10 | 78 ± 1 | 105 ± 2 | 1.3 |
| 80.5 | 0.40 | 86 ± 3 | 154 ± 3 | 1.7 |
| 100.3 | 0.10 | 94 ± 1 | 119 ± 5 | 0.9 |

[a] $\mu = 0.4$ *M*, $\lambda$ 510 m$\mu$, $[MnO_4^-] = 4.00 \times 10^{-4}$ *M*. [b] $[MnO_4] = 20.0 \times 10^{-4}$ *M*.

In order to determine the effect of structure on the rate of reaction, 11 additional substrates were examined in the same fashion as for crotonate ion. The substrates include the aliphatic acids: acrylic, vinylacetic,

---

[7] A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, 1628 (1925); J. E. Coleman, C. Ricciuti, and D. Swern, *J. Am. Chem. Soc.*, 78, 5342 (1956).

[8] J. W. McBain, "Colloid Science," D. C. Heath and Co., Boston, Mass., 1950, Chapter 17.

*trans*-2-pentenoic, *trans*-4-bromocrotonic, *trans*-3-pentenoic, and 4-pentenoic; the cinnamic acid derivatives: *trans*-cinnamic, *trans*-*p*-methoxycinnamic, *trans*-*p*-methylcinnamic, and *trans*-*p*-chlorocinnamic; and the unsaturated alcohol, allyl alcohol. The results are summarized in Table III, which gives both values for $k_1$ and estimates for $k_2$. It should be noted that, where values of $k_1$ have been determined in both neutral and basic solution, they always agree to within 5% of each other. This has been taken as the per cent error in $k_1$ for all determinations and has been used in calculating the uncertainties in the activation parameters given in Table IV.

**Table III.** Summary of Kinetic Results for Alkene Substrates

| Alkene | pH | Temp, °C | $N^a$ | Approx range, [alkene] × $10^4$ $M$ | $k_1$, $M^{-1}$ sec$^{-1}$ | Range of $k_2$ × $10^{-3}$ $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|---|---|
| Allyl alcohol | 13 | 25.0 | 6 | 4–80 | 137 ± 7 | 6–8 |
| | 6.5 | 25.0 | 4 | 10–60 | 140 ± 7 | |
| | 13 | 0.5 | 5 | 20–100 | 38 ± 2 | |
| | 6.5 | 0.5 | 5 | 20–100 | 43 ± 2 | |
| Acrylate | 13 | 25.0 | 8 | 4–26 | 330 ± 17 | |
| | 13 | 0.5 | 5 | 10–50 | 133 ± 7 | 15–18 |
| Crotonate | 13 | 25.0 | 14 | 1–40 | 220 ± 11 | 12–23 |
| | 6.5 | 25.0 | 5 | 10–60 | 232 ± 11 | |
| | 13 | 0.5 | 7 | 20–100 | 95 ± 5 | 0.9–3.5 |
| | 6.5 | 0.5 | 5 | 20–100 | 100 ± 5 | |
| Vinylacetate | 13 | 25.0 | 9 | 2–80 | 111 ± 6 | 7–15 |
| | 13 | 0.5 | 4 | 10–80 | 38 ± 2 | 2–11 |
| 4-Bromocrotonate | 13 | 25.0 | 5 | 4–20 | 325 ± 16 | 11–16 |
| 2-Pentenoate | 13 | 25.0 | 5 | 20–60 | 242 ± 12 | 7.6–12 |
| 3-Pentenoate | 13 | 25.0 | 5 | 5–30 | 455 ± 23 | 6.1–12 |
| 4-Pentenoate | 13 | 25.0 | 5 | 5–40 | 167 ± 8 | 7.1–12.5 |
| | 13 | 0.5 | 5 | 5–80 | 55 ± 3 | 8.1–14 |
| Cinnamate | 13 | 25.0 | 12 | 3–24 | 503 ± 25 | 9.1–20 |
| | 6.5 | 25.0 | 4 | 5–20 | 490 ± 25 | |
| | 13 | 0.5 | 7 | 5–40 | 280 ± 14 | 1.4–4.2 |
| | 6.5 | 0.5 | 5 | 10–80 | 276 ± 14 | |
| *p*-Methylcinnamate | 13 | 0.5 | 3 | 10–40 | 278 ± 14 | 0.9–2.4 |
| | 6.5 | 0.5 | 3 | 10–40 | 260 ± 14 | |
| *p*-Methoxycinnamate | 13 | 0.5 | 3 | 10–40 | 264 ± 14 | 1.3–3.3 |
| | 6.5 | 0.5 | 3 | 10–40 | 272 ± 14 | |
| *p*-Chlorocinnamate | 13 | 0.5 | 3 | 10–40 | 302 ± 15 | 0.4–3.1 |
| Oleate | 13 | 25.0 | 40 | 1–400 | 70 | |

[a] Number of experiments.

**Table IV.** Activation Parameters for the Permanganate Oxidation of Some Alkenes

| Substrate | $\Delta F^{\ddagger}$, kcal/mole | $\Delta H^{\ddagger}$, kcal/mole | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|
| Allyl alcohol | 14.6 | 7.5 ± 0.7 | −24 ± 2 |
| Acrylate ion | 14.1 | 5.3 ± 0.7 | −30 ± 2 |
| Crotonate ion | 14.3 | 4.8 ± 0.7 | −32 ± 2 |
| Vinylacetate ion | 14.8 | 6.4 ± 0.7 | −28 ± 2 |
| 4-Pentenoate ion | 14.5 | 6.6 ± 0.7 | −27 ± 2 |
| Cinnamate ion | 13.9 | 3.3 ± 0.7 | −36 ± 2 |

The data on the effect of substituents permit several interesting comparisons. With the pentenoic acids (C—C—C═C—COOH, $k_1$ = 242; C—C═C—C—COOH, $k_1$ = 455; C═C—C—C—COOH, $k_1$ = 167) it appears that deconjugation and methyl substitution are both somewhat favorable. The butenoic acids (C—C═C—COOH, $k_1$ = 220; C═C—C—COOH, $k_1$ = 111) have rate constants which are similar to the correspondingly substituted pentenoic acid. If one compares the alkyl-substituted conjugated acids (C—C—C═C—COOH, $k_1$ = 242; C—C═C—COOH, $k_1$ = 220; C═C—COOH, $k_1$ = 320) it appears that methyl substitution hinders the reaction of the conjugated double bond. Finally, a comparison of crotonic acid ($k_1$ = 200) with cinnamic acid ($k_1$ = 503) indicates that phenyl conjugation accelerates the reaction.

In the hope that the effect of substituents might reveal something about the nature of the activated complex, we have examined the oxidations of *p*-methyl-, *p*-methoxy-, and *p*-chlorocinnamic acid. All reacted at essentially the same rate as cinnamic acid itself, showing the reaction to be remarkably insensitive to electronic effects. The relatively small rate increase on going from crotonic acid to 4-bromocrotonic acid indicates the same to be true for the aliphatic acids.

Structural effects which stabilize the double bond (phenyl conjugation and methyl substitution) usually give a small rate acceleration. This is contrary to expectation for a reaction which does not respond to electronic effects since stabilization of the reactants would be expected to increase the activation energy. Apparently, the activated complex is stabilized somewhat more than the reactant. It is difficult to see how this comes about if charges are not developed in the activated complex.

The work of Huisgen[9] on 1,3-dipolar additions provides an analogy for the structural effects observed here. The 1,3-dipolar additions are accelerated by alkyl substitution and by phenyl or carboxyl conjugation, and are characterized by $\rho$ values close to zero. There appears to be a remarkable similarity between the 1,3-dipolar addition reactions and the permanganate oxidation.

Although the kinetics of the initial reaction of permanganate with alkenes have been studied in some detail, little is known about the subsequent steps. Further data on the kinetics of the second step in the reaction as well as information on the effect of pH on the products of the reactions of crotonic and cinnamic acids will be presented subsequently.

## Experimental Section

**Materials.** Allyl alcohol (Eastman) was distilled at atmospheric pressure (bp 96–98°) and further purified by preparative vpc (silicone 710 column at 60°). Acrylic acid (Matheson) was distilled at atmospheric pressure and further purified by fractional freezing, keeping only the material which was solid at 12°. *trans*-Crotonic acid (Eastman) was recrystallized twice from purified *n*-hexane and once from distilled water, and dried over phosphorus pentoxide (mp 72.0–72.5°). Vinylacetic acid was prepared as described[10] and was separated from residual crotonic acid by preparative vpc silicone (710 column at 100°). *trans*-3-Pentenoic acid was prepared by the method of Linstead[11] and had bp 97–98° (20 mm). It was further purified by preparative vpc (silicone 710, 150°). *trans*-2-Pentenoic acid was prepared by the method of Kurien,

---

(9) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

(10) J. V. Supniewski and P. L. Salzberg, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 46; E. Riety, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 851.

(11) R. P. Linstead, *J. Chem. Soc.*, 557 (1933).

*et al.*,[12] and had bp 106–110° (20 mm). It was further purified by redistillation, fractional freezing keeping only material which was solid at 9°, followed by preparative vpc (silicone 710, 150°). *trans*-*p*-Chlorocinnamic acid was prepared by mixing 70 g (0.5 mole) of *p*-chlorobenzaldehyde with 52 g (0.5 mole) of malonic acid and 2 ml of pyridine. The mixture was heated on a steam bath for 24 hr. The solid was collected and washed twice with methanol, giving 84 g (92%) of almost pure acid. Before use it was recrystallized three times from methanol (mp 243–245°). *trans-p*-Methylcinnamic acid was prepared in the same way starting with *p*-tolualdehyde. After three recrystallizations from methanol it had mp 197–198°. *trans-p*-Methoxycinnamic acid was prepared (73% yield) in the same way starting with anisaldehyde. After three recrystallizations from methanol it had mp 171–173°. *trans*-Cinnamic acid (Eastman) was recrystallized three times from a chloroform–hexane mixture and had mp 132–133°. 4-Pentenoic acid (K & K laboratories) was shown to be pure by vpc and was used without further purification. *trans*-4-Bromocrotonic acid was prepared by treating 86 g (1.0 mole) of recrystallized crotonic acid with 110 ml (1.5 moles) of purified thionyl chloride on a steam bath for 2 hr. Distillation gave 79 g (76%) of crotonyl chloride, bp 33–37° (18 mm). To a mixture of 23.5 g (0.12 mole) of N-bromosuccinimide in 200 ml of carbon tetrachloride was added 13 g (0.12 mole) of crotonyl chloride. The mixture was heated until all the N-bromosuccinimide had gone into solution (about 3 hr) and was then filtered. To the filtrate was added 100 ml of water, and the mixture was heated until all the carbon tetrachloride had boiled off. The aqueous layer was heated an additional 15 min and then cooled. The precipitate was filtered and recrystallized twice from hexane, giving 2 g (10%) of 4-bromocrotonic acid, mp 72–74°. Oleic acid (Fisher Scientific Co., free from linoleic acid) had mp 3–4° and was used without further purification.

Potassium phosphate buffer solutions of pH 6.5 were prepared as stock solutions with an ionic strength of 0.8 *M* by dissolving 38.8 g (0.140 mole) of monobasic potassium phosphate (analytical grade) and 38.7 g (0.087 mole) of dibasic potassium phosphate trihydrate (analytical grade) in water and diluting to 1 l. total volume. Potassium permanganate stock solutions, $2.00 \times 10^{-2}$ *M*, were prepared from Acculute volumetric standard solutions. These stock solutions were standardized against arsenous oxide and were found to remain unchanged for 4 or 5 months when kept in the dark.

**Kinetic Method.** The rate of oxidation by permanganate was determined by following spectrophotometrically the disappearance of permanganate. The stopped-flow reactor which was used employed a conventional design and both the storage and reacting solutions could be well thermostated. The reactor employed a 10-cm cell with a total volume of 3 ml. Approximately 0.2 sec was required to half-fill the cell. A Beckman DU spectrometer and associated electronics was employed, and the output of the energy recording adapter was recorded using a Honeywell-Brown strip-chart recorder having a 0.25-sec full-scale response and chart speeds up to 120 in./min. The photomultiplier was used instead of the regular photocell, and the usual load resistor–capacitor combination was replaced with a 1-megohm resistor in order to decrease the time constant of the detector circuit. The zero level was set using the shutter and dark current control; 100% transmission was set using distilled water in the cell.

---

[12] P. N. Kurien, K. C. Pandya, and V. R. Surange, *J. Indian Chem. Soc.*, **11**, 823 (1934).

---

# Kinetics of the Nitric Acid Oxidation of Benzyl Ethers to Benzaldehydes

**Yoshiro Ogata and Yasuhiko Sawaki**

*Contribution No. 93 from the Department of Applied Chemistry,*
*Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.*
*Received June 3, 1966*

**Abstract:** The nitric acid oxidation of benzyl ethers has been studied kinetically in aqueous dioxane. The oxidation is initiated by a small amount of nitrous acid and follows first-order kinetics with respect to the ether. The rate of oxidation is in most cases independent of either nitric acid (over 0.5 *M*) or nitrous acid, while the oxidation with more dilute (below 0.5 *M*) nitric acid contains a term of nitric acid in the rate equation. The oxidation is accelerated by increasing the acidity of media; the plot of log $k_1$ *vs.* $-H_0$ gives a straight line with a slope of 1.0. The rate constant also increases with increasing dioxane content in the solvent. The apparent energy and entropy of activation are 31–34 kcal/mole and 10–13 eu, respectively. The substituent effect in the benzyl ring satisfies Hammett's equation, giving a $\rho$ value of $-1.9$. A polar effect is also observed with the substituents in alkyl group, the order of reactivity being *i*-Pr > Et > Me > $C_6H_5$. A mechanism which involves the benzyl hydrogen abstraction by the conjugate acid of nitrogen dioxide is postulated and discussed.

On treatment of benzyl halide with dilute nitric acid, the halide is hydrolyzed to benzyl alcohol and the alcohol is oxidized to benzaldehyde.[1,2] The nitric acid oxidation of benzyl alcohol to benzaldehyde may be explained by a radical mechanism involving the abstraction of a benzyl hydrogen atom with nitrogen dioxide.[3] Only a few investigators have reported on the heterogeneous reaction of benzyl ethers with nitric acid.[4,5]

It was found that the oxidation of benzyl ether is difficult with pure nitric acid, but it may readily be started by addition of a small amount of sodium nitrite, resulting in a high yield (over 95%) of benzaldehyde. The present paper describes the kinetic study dealing with the effects of nitrous acid, the acidity of media, temperature, and substituent on the rate of

$$ArCH_2OR \xrightarrow{HNO_3} ArCHO \qquad (1)$$

---

[1] Y. Ogata, Y. Sawaki, H. Tezuka, and F. Matsunaga, *Kogyo Kagaku Zasshi*, **69**, 901 (1966).

[2] I. S. Bengelsdorf, *J. Org. Chem.*, **23**, 242 (1958).

[3] Y. Ogata, Y. Sawaki, F. Matsunaga, and H. Tezuka, *Tetrahedron*, **22**, 2655 (1966).

[4] K. A. Bogdanov and V. N. Antonova, *Maslob.-Zhir. Prom.*, **27**, 32 (1961); *Chem. Abstr.*, **55**, 15395 (1961).

[5] B. Reichert and W. Hoss, *Arch. Pharm.*, **280**, 157 (1942); *Chem. Abstr.*, **37**, 2001 (1943).