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Kinetics of the Base-Catalyzed Permanganate Oxidation of Benzaldehyde

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The kinetics of the base-catalyzed permanganate oxidation of benzaldehyde have been reexamined. The rate is proportional to the first power of the aldehyde and permanganate concentrations, and there are terms that are zero order, first order, and second order in hydroxide ion. The reaction has an isotope effect, and the effect of substituents gives $\rho = +1.58$. The possible mechanisms for the reaction are discussed in the context of ab initio calculations at the B3P86/6-311+G** and MP2/6-31G* theoretical levels, and both one- and two-electron processes are possible. Benzaldehyde hydrate dianion is calculated to have a remarkably small C−H bond dissociation energy.

Some years ago, we reported an investigation of the kinetics of the permanganate oxidation of benzaldehyde.[2] The pH−rate profile had three regions corresponding to an acid-catalyzed reaction below about pH 5, an uncatalyzed reaction from about pH 6 to pH 9, and a base-catalyzed reaction above pH 10. The kinetics of the latter reaction could not be determined precisely because of the high rate constants and the analytical method used. We now wish to report an extended investigation of the base-catalyzed reaction using a stopped-flow reactor to measure spectrometrically the change in permanganate concentration with time.

The reaction was studied in basic aqueous solutions under pseudo-first-order conditions with permanganate as the limiting reagent. Under these conditions, manganate is the inorganic product. Good first-order behavior was noted through better than 75% reaction, and the rate constant did not change significantly with a 3-fold change in permanganate concentration (Table 1). For the remainder of the experiments, a permanganate concentration of 3×10^{-4} M was used.

Table 1. Effect of Permanganate Concentration on the Rate of Oxidation[a]

$[MnO4^-] \times 10^4$	$k_1 \times 10^{-2}$ s^{-1}	k (av)
2.5	6.02	
	6.13	
	6.05	6.08 ± 0.05
3.0	6.29	
	6.37	
	6.40	
	6.25	6.33 ± 0.06
5.0	6.38	
	6.41	
	6.29	
	6.61	6.42 ± 0.09
7.5	6.44	
	6.33	
	6.82	6.54 ± 0.16

[a] $\lambda = 522$ nm, $T = 25.0$ °C, $[HO^-] = 0.25$ M, pH = 13.4, $\mu = 0.4$, $[PhCHO] = 9.8 \times 10^{-3}$ M.

The effect of benzaldehyde concentration on the rate of reaction was determined using a 10-fold change in concentration. The data are summarized in Figure 1. A small intercept is found on extrapolation to zero benzaldehyde concentration. This in part results from the base-catalyzed decomposition of permanganate.[3] However, it appears somewhat larger than might be expected from this source.

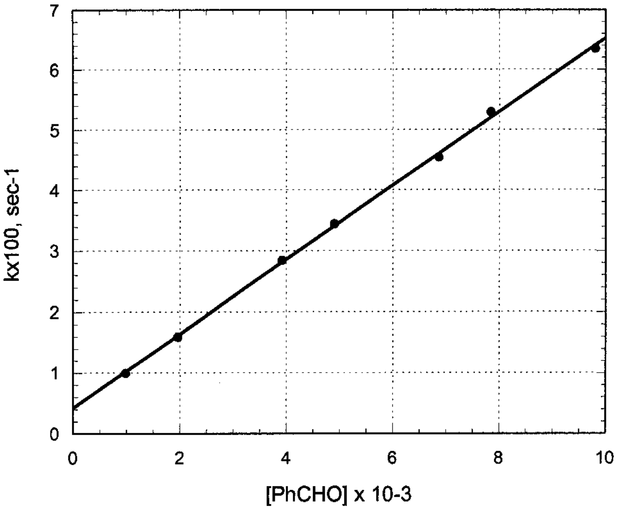

Figure 1. Effect of benzaldehyde concentration on the pseudo-first-order rate constants for the disappearance of permanganate ion.

The effect of hydroxide ion concentration also was determined, giving the data summarized in Figure 2. A linear relationship was not obtained. The curvature suggests a kinetic form of the type

$$k_{\mathrm{obs}} = k_1 + k_2[\mathrm{HO}^-] + k_3[\mathrm{HO}^-]^2$$

A least-squares fit of the experimental data to the above equation gave $k_1 = 2.06 \times 10^{-2}$, $k_2 = 14.9 \times 10^{-2}$, and $k_3 = 11.1 \times 10^{-2}$ for an aldehyde concentration of 9.8×10^{-3} M. The solid line in the figure is calculated using these constants and can be seen to give an excellent fit. The dotted line represents k_2 alone. The kinetics of the oxidation of benzaldehyde may now be expressed as

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(2) (a) Wiberg, K. B.; Stewart, R. *J. Am. Chem. Soc.* **1955**, *77*, 1786. (b) Tompkins, F. C. *Trans. Faraday Soc.* **1943**, *39*, 280.

(3) Jezowska-Trzebiatowska, B.; Kalecinski, J. *Chem. Abstr.* **1960**, *54*, 19122.

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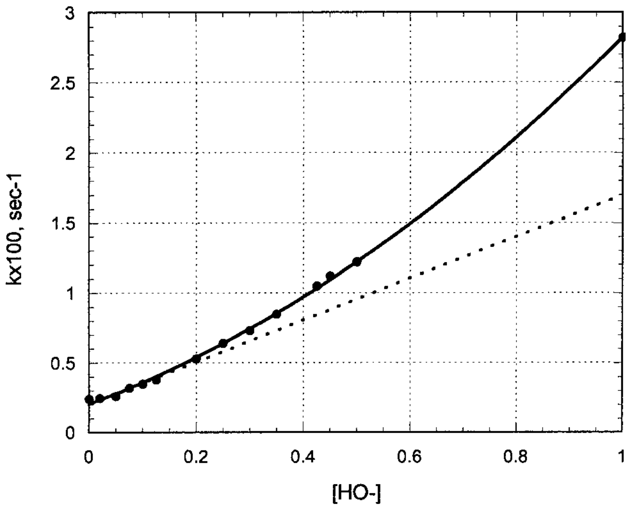


Figure 2. Effect of hydroxyl ion concentration on the pseudo-first-order rate constants for the disappearance of permanganate ion with a benzaldehyde concentration of 9.8 × 10^{-3} M. The solid line gives the best fit to the data, and the dashed line indicates the contribution of just k_1 and k_2.

Table 2. Kinetic Isotope Effect in the Oxidation of Benzaldehyde

$[HO^-]$	$k_H \times 10^2\ s^{-1}$	$k_D \times 10^2\ s^{-1}$	k/k_D
0.01	2.52 ± 0.04	1.14 ± 0.08	2.2
0.05	2.77 ± 0.02	1.21 ± 0.02	2.2
0.25	6.29 ± 0.02	2.05 ± 0.02	3.1
0.35	8.57 ± 0.02	2.44 ± 0.02	3.5
0.50	12.63 ± 0.03	3.59 ± 0.02	3.5

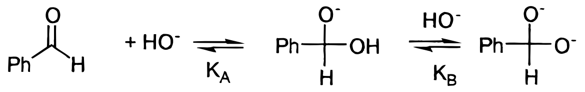
$$-d[MnO_4^-]/dt = k_1[PhCHO][MnO_4^-] + k_2[PhCHO][MnO_4^-][HO^-] + k_3[PhCHO][MnO_4^-][HO^-]^2$$

where $k_1 = 2.10$ L mol^{-1} s^{-1}, $k_2 = 15.2$ L^2 mol^{-2} s^{-1}, and $k_3 = 11.3$ L^3 mol^{-3} s^{-1}.

The kinetic isotope effect was examined using benzaldehyde-*d*, giving the data in Table 2. The value of k_H/k_D appears to increase somewhat on going from 0.01 to 0.25 M base and then levels off. The first two values may, however, be somewhat in error because the rates were so slow that formation of manganese dioxide began to be a problem.

Finally, the effect of substituents was examined using a set of eight aldehydes and 0.25 M sodium hydroxide. The results are summarized in Figure 3. A fairly good linear relationship was obtained with $\rho = +1.54$.

The data suggest that benzaldehyde initially adds hydroxyl ion and that the ion thus formed may be further deprotonated in an equilibrium step to form the dianion:



All three species (benzaldehyde, the monoanion, and the dianion) may then be attacked by permanganate in rate-determining steps. It was of interest to estimate the rate constants for the rate-determining steps. This requires information on the equilibrium constants K_A and K_B. K_A has been measured in aqueous solution and was found to be 0.18, and the ρ value for the addition was +2.24.[4] Thus, the rate constant for the reaction of the monoanion with permanganate is 84 L mol^{-1} s^{-1}, and most of the substituent effect on the rate of reaction may be attributed to the formation of the monoanion. The rate-determining step has a small negative value of ρ.

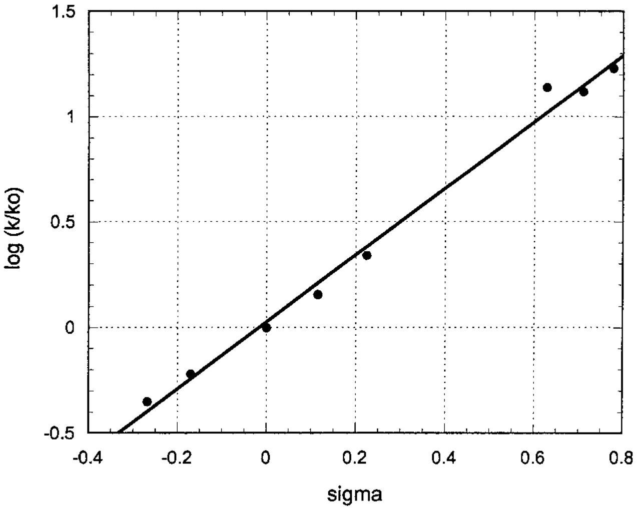
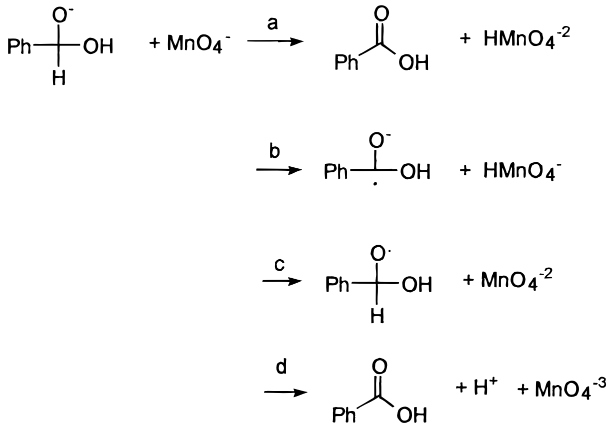


Figure 3. Effect of substituents on the rate constants for the permanganate oxidation of benzaldehyde in 0.25 M sodium hydroxide solutions. From left to right, the substituents are *p*-MeO, *p*-Me, H, *m*-MeO, *p*-Cl, *p*-CN, *m*-NO_2, and *p*-NO_2.

The pK_a of the monoanion is not known, but because it has a negative charge its acidity should be considerably less than that of an alcohol. If it were estimated to be 20, K_B would be on the order of 10^{-6}, and the rate constant for the reaction of the dianion with permanganate would be on the order of 10^8 L mol^{-1} s^{-1}. This is close to diffusion controlled.

There are four possible reaction paths for the anion–permanganate reactions: (a) hydride donation from the anion to permanganate; (b) hydrogen atom donation from the anion to permanganate; (c) one-electron transfer from the anion to permanganate; and (d) two-electron transfer from the anion to permanganate with loss of the aldehyde hydrogen as a proton.



Paths b and c are one-electron transfers giving an intermediate that would react with another permanganate to give the product, benzoic acid. Paths a and d are two-electron processes that give benzoic acid directly along with Mn(V) that would react with another per-

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(4) Greenzaid, P. *J. Org. Chem.* **1973**, *38*, 3164.

Table 3. Calculated Energies

Total Energies (H) and Zero-Point Energies (kcal/mol)

compound	B3P86		s^2	MP2	s^2	PMP2	ZPE[a]
	$\epsilon = 1$	$\epsilon = 80$					
$PhCH(OH)_2$	−423.30974	−423.31835		−420.69582			83.6
$PhCH(OH)O^-$	−422.7274	−422.81387		−420.09920			74.5
$PhCHO_2^{2-}$	−421.94593	−422.25068		−419.27707			65.0
$PhC(OH)_2$	−422.64446	−422.65671	0.776	−420.04346	0.766	−420.04560	73.1
$PhC(OH)O^-$	−422.11418	−422.19381	0.763	−419.49366	1.035	−419.51153	66.4
$PhCO_2^{2-}$	−421.41830	−421.66661	0.756	−418.76404	0.809	−418.76903	58.2

C−H Bond Dissociation Energies (kcal/mol)[b]

compound	PMP2	B3P86, $\epsilon = 1$	B3P86, $\epsilon = 80$
$PhCH(OH)_2$	85	93	91
$PhCH(OH)O^-$	48	63	68
$PhCHO_2^{-2}$	0	11	46

[a] HF/6-31G* zero-point energies scaled by 0.893. [b] The MP2/6-31G* energy of a hydrogen atom is 0.49823 H. DFT models lead to an incorrect energy for a hydrogen atom because they attempt to introduce correction for electron correlation in this atom, for which there cannot be any such energy. Thus, the correct value, 0.50000 H, was used.

manganate to give Mn(VI). Similar pathways may be written for the dianion.

Path c seems relatively unlikely because it does not directly involve the aldehyde hydrogen and could only give a secondary isotope effect. Thus, this process is not likely to give a kinetic isotope effect of 3.5, as has been observed for the reaction. It is not possible to distinguish between the remaining paths on the basis of just the available experimental data.

Thus, we have carried a series of ab initio calculations for the species that are involved. If the one-electron transfer process c were involved, the conversion of the monoanion to the dianion would have to result in a marked reduction in the C−H bond dissociation energy to account for the much more rapid reaction of the dianion.[5] Geometry optimizations were carried out at the B3P86/6-311+G** level,[6] which makes use of a relatively flexible basis set including diffuse functions that have been found to be important in describing anions and includes correction for the effects of electron correlation. In addition, density functional theory models have been found to minimize spin contamination in free radicals.[7] The results are summarized in Table 3.

Benzaldehyde hydrate has a calculated C−H bond dissociation energy similar to that for toluene (88 kcal/mol). The monoanion has a much smaller calculated dissociation energy, and that for the dianion is remarkably small. It seemed possible that the density functional method might give an anomalous energy for the dianion radical. Thus, geometry optimizations were carried out at the MP2/6-31G* level, and the calculated energies are included in Table 3. The B3P86 and MP2 derived dissociation energies differ by about 10 kcal/mol. However, the changes in BDE on going from benzaldehyde hydrate to the monoanion and the dianion are the same in both series, and both predict that the dianion will have a low C−H dissociation energy.

Dianions are generally unstable in the gas phase and eject an electron, forming a monoanion. They are, however, often stable in polar solvents that reduce their electrostatic energies by over 100 kcal/mol. The effect of a polar solvent was examined using the SCIPCM reaction field model,[8] and the results are included in Table 3. In the case of anions, the electron density distribution is fairly diffuse. As a result, a significant part of the total electron density lies outside the 0.0004 e/au^3 isodensity surface that is usually taken to give the size and shape of the solute. As a result, it was necessary to scale the charge so that all would lie within the solvent cavity. It can be seen that the calculated dissociation energies for benzaldehyde hydrate and the monoanion are not much affected by going from the gas phase to a polar medium. In the case of the dianion, the calculated BDE increases significantly on going to a polar medium, and as noted below, this is due to the two negative charges being better dispersed in the dianion radical than in the dianion. The BDE is, nevertheless, significantly lower than that for the monoanion. Further, only part of the charge redistribution can occur in the transition state for C−H bond cleavage in the hydrate dianion. Thus, the kinetic effect of going from the hydrate monoanion to the dianion should be between the gas phase and solution calculated values.

The low dissociation energy of the dianion makes process c a possible mechanism for the rate-determining step. Process a is also possible because the dianion would be a better hydride transfer reagent than the monoanion. Process d is not excluded by any of the data. This brings us back to the old question as to whether elements such as manganese are able to accept two electrons in one step, or if they are required to accept electrons one at a time. Further calculations are being carried out to locate the transition state for the reaction and to examine its electron-transfer characteristics, taking the solvent into account. These calculations will also allow the predication of the kinetic hydrogen isotope effect, which may be compared with the observed value.

The stability of the dianion radical, $PhCO_2{\bullet}^{2-}$, is interesting in itself. To gain information on its bonding and electron density distribution, its MP2 wave function was examined using Bader's theory of atoms in molecules.[9] Both the AIM analysis and the Mulliken popu-

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(5) Gardner, K. A.; Mayer, J. M. *Science* **1995**, *269*, 1849. These authors have shown that the rates of permanganate oxidation of C−H bonds are related to the bond dissociation energies.

(6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 5048.

(7) Wiberg, K. B.; Cheeseman, J. R.; Ochterski, J.; Frisch, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6535

(8) Foresman, J.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098.

(9) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

lationanalysis agreed that the CO_2 group had a unit negative charge (i.e., it is an ordinary carboxylate group), and the phenyl ring had the odd electron and a negative charge. Thus, the low dissociation energy derives at least in part from the possibility for transferring the odd electron of the radical as it is formed to the phenyl ring, thus separating the two negative charges.

This observation may prove significant in the context of determining via computations whether two electrons may be simultaneously transferred to manganese. In most cases, if one-electron transfers were operative, the movement of the first electron could be closely followed by the second, and it would be difficult to observe the separate steps. However, with benzaldehyde hydrate dianion, one-electron transfer to manganese might be immediately followed by transfer of the second electron to the phenyl ring. If this were found, it would demonstrate the operation of one-electron transfers.

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