# Permanganate Oxidations. II. Kinetics and Mechanism of the Oxidation of Cyclohexanenitronate and Cyclopentanenitronate Anions[1]

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*Received November 20, 1968*

The kinetics of the permanganate oxidation of cyclohexanenitronate (I) and cyclopentanenitronate (II) anions were investigated *via* spectrophotometric stopped-flow techniques from pH 12.5 to 13.5. The reactions were first order in nitronate anions and in permanganate, and zero order in hydroxide ion. A positive salt effect was observed with I, and I was oxidized six times faster than II. $\Delta H^{\ddagger}$ was 7.45 kcal/mol for I and 10.5 kcal/mol for II, and $\Delta S^{\ddagger}$ was −27.8 eu for I and −20 eu for II. The data are consistent with orbital rehybridization in the rate-determiming step which suggests an attack of permanganate at the carbon of the carbon-nitrogen double bond of the nitronate anion.

Very few bimolecular reactions in organic chemistry are characterized by rate constants larger than 1 l. mol$^{-1}$ sec$^{-1}$. Recently Wiberg and Geer[2] and Freeman and Yeramyan[1] have reported second-order rate constants in excess of 150 l. mol$^{-1}$ sec$^{-1}$ for the permanganate oxidation of alkenes and the anion of phenylnitromethane, respectively. Another rapid reaction of this type is the permanganate oxidation of cycloalkylnitronate anions. Although Schechter and Williams[3-6] have investigated the scope of the permanganate oxidation of nitro compounds to carbonyl compounds, only one report[1] has appeared concerning the kinetics of this extremely rapid reaction. The purpose of the work reported herein was to investigate the kinetics and mechanism of the permanganate oxidation of cyclohexanenitronate (I) and cyclopentanenitronate (II) anions. In this paper we present a detailed kinetic study of I and II.

## Experimental Section

**Reagents.**—Distilled water was purified by passing through an ion-exchange cartridge (Type R-2, Illinois Water Treatment Co., Rockford, Ill.).

Mallinckrodt reagent grade sodium chloride was used without further purification to adjust ionic strength. Acculute standard volumetric potassium hydroxide ($CO_2$ free) concentrate was diluted to the specified volume for the desired pH. The pH of the solutions were taken as those measured potentiometrically. Potassium permanganate stock solutions, $2.00 \times 10^{-2}$ *M*, were prepared from Acculute standard volumetric solutions. The stock solution was stored under nitrogen and was standardized when not used frequently. (The absorbancy index was checked for permanganate before each set of kinetic runs.) These stock solutions did not deteriorate for 5-6 months when kept in the dark. Deionized water was used to prepare standard stock solutions.

**Nitrocyclohexane** (III) (Aldrich) was distilled at reduced pressure immediately before use. Nitrocyclopentane (IV) was prepared according to the procedure of Kornblum and Powers:[7] bp 62-63° (8 mm); $n^{20}\text{D}$ 1.4531 [lit.[7] bp 48° (1 mm); $n^{20}\text{D}$ 1.4539].

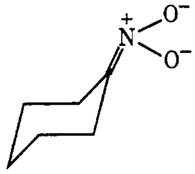
**Apparatus and Procedures.**—Because of the short reaction time, the rates were determined by following spectrophotometrically the disappearance of permanganate in a stopped-flow reactor[8] which permitted study of reactions with half-lives as low as 0.4 sec. A Beckman Model DU instrument was modified with an energy-recording adapter so that the signal output could be followed with a Bristol strip-chart recorder having a 0.20-sec full-scale response and chart speeds up to 120 in./min. The stopped-flow reactor was designed so that the storage and reacting solutions could be well thermostated. A 4- or 10-mm Pyrex cell with a volume of 1.2 or 3 ml was employed. The time required to half fill the cell with the mixed reaction solution was less than 0.2 sec.

All studies were performed under pseudo-first-order conditions, and the rates were followed until the reactions were 75-90% complete. The rate constants were obtained from plots of $-\ln [\log (T_\infty/T)]$ against time and were calculated on an IBM 360 computer.[9] The rate constants given in the tables are the average of two or more determinations, and the deviations are the *mean* deviations for the set of runs. The small deviations suggest a reasonably good degree of accuracy.

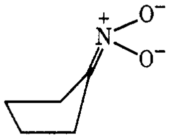
## Results

**Stoichiometry.**—The stoichiometry of the reaction has been verified by Schechter and Williams.[3] Ultraviolet spectral determinations with nitrocyclohexane III and nitrocyclopentane IV at pH 13.0 showed that both were almost completely converted into the relatively stable nitronate ions (I and II).[10-13] To ensure that permanganate did not enter into subsequent oxidation reactions with the enolic forms of the products or nitrite ion, the rate constants were calculated three times using the data to the first half-life, to the second half-

$$3RC{=}NO_2K + 2KMnO_4 + H_2O \longrightarrow 3R_2C{=}O + 2MnO_2 + 3KNO_2 + 2KOH \quad (1)$$



I



II

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[1] Previous paper in series: F. Freeman and A. Yeramyan, *Tetrahedron Lett.*, 4783 (1968).

[2] K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **87**, 5202 (1965); **88**, 5827 (1966).

[3] H. Schechter and F. T. Williams, *J. Org. Chem.*, **27**, 3699 (1962).

[4] Although previous workers[3] used a buffered KOH–$MgSO_4$ system, the reactive species presumably is the nitronate anion. Other examples of nonbuffered systems have been reported.[3,5,6]

[5] Additional references for the permanganate oxidation of salts of nitro compounds to carbonyl compounds, in excellent yields, are given in ref 3.

[6] (a) S. S. Nametkin and E. Posdnjakova, *J. Russ. Phys. Chem. Soc.*, **45**, 1420 (1913); (b) S. S. Nametkin and O. Madaeff-Ssitscheff, *Chem. Ber.*, **59**, 370 (1926).

[7] N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957).

[8] Modification of an original design by Professor K. B. Wiberg, Department of Chemistry, Yale University, New Haven, Conn.

[9] We wish to thank the Western Data Computing Center, University of California, Los Angeles, Los Angeles, Calif., for making computer time available to us.

[10] Ultraviolet spectroscopy showed that III and IV were more than 98% converted into I (231 mμ) and II (226 mμ), respectively, under kinetic conditions. See also ref 11.

[11] (a) F. T. Williams, Jr., P. W. K. Flanagan, W. V. Taylor, and H. Schechter, *J. Org. Chem.*, **30**, 2674 (1965). (b) P. W. K. Flanagan, H. W. Amburn, H. W. Stone, J. G. Traynham, and H. Schecter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969).

[12] M. H. Hawthorne, *ibid.*, **79**, 2510 (1957).

[13] A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962).

life, and then to the third half-life. By comparing these values, any deviation from linearity was readily observed. A typical kinetic plot is shown in Figure 1.

**Cyclohexanenitronate Anion (I).**—The kinetic data for the oxidation of I are summarized in Table I. A plot of $k_\psi$ *vs.* concentration of I gives a straight line that goes through the origin, indicating the rate of oxidation to have a first-order dependence on I. The constancy of the values of $k_2$ over a tenfold range of hydroxyl ion concentration at constant cyclohexanenitronate anion and permanganate concentrations indicates a zero-order dependence on hydroxide ion. At constant hydroxide ion and cyclohexanenitronate anion concentrations, the rate constants do not alter with changing permanganate concentrations which indicates a first-order dependence on permanganate. These data suggest the following rate law.

$$\frac{-\mathrm{d}[\mathrm{MnO_4}^-]}{\mathrm{d}t} = 2k_2[\text{cyclohexanenitronate anion}][\mathrm{MnO_4}^-]$$

TABLE I

RATE DATA FOR THE OXIDATION OF CYCLOHEXANENITRONATE ANION

($\mu$ = 0.5 *M*, λ 522 mμ, *T* = 1.0 ± 0.02°, 10-mm cell)

| [Nitrocyclohexane] × $10^4$ *M* | [OH$^-$], *M* | [MnO$_4^-$] × $10^4$ *M* | $2k_\psi$[a] × $10^2$ sec$^{-1}$ | $2k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|
| 15.0 | 0.10 | 4.00 | 51 ± 1 | 337 |
| 20.0 | 0.10 | 4.00 | 66 ± 1 | 330 |
| 25.0 | 0.10 | 4.00 | 83 ± 1 | 330 |
| 30.0 | 0.10 | 4.00 | 103 ± 4 | 345 |
| 40.0 | 0.10 | 4.00 | 137 ± 1 | 342 |
| 45.0 | 0.10 | 4.00 | 148 ± 2 | 328 |
| 55.0 | 0.10 | 4.00 | 176 ± 2 | 321 |
| 40.0 | 0.032 | 4.00 | 112 ± 4 | 279 |
| 40.0 | 0.05 | 4.00 | 117 ± 2 | 293 |
| 40.0[b] | 0.08 | 4.00 | 116 | 291 |
| 40.0 | 0.32 | 4.00 | 117 ± 3 | 292 |
| 40.0[c] | 0.10 | 6.00 | 121 ± 3 | 301 |
| 40.0[c] | 0.10 | 8.00 | 119 ± 1 | 297 |
| 40.0[c] | 0.10 | 10.00 | 120 ± 1 | 301 |
| 40.0[c] | 0.10 | 12.00 | 117 ± 1 | 291 |
| 40.0[c] | 0.10 | 14.00 | 120 ± 3 | 301 |

[a] Pseudo-first-order rate constant with mean deviation. [b] One experiment. [c] 4-mm cell used.

**Salt Effects.**—Table II shows that there is a positive salt effect in the permanganate oxidation of I. This is consistent with the Debye–Hückel theory which predicts that a reaction between like charged ions will be accelerated by an increase in ionic strength.[14]

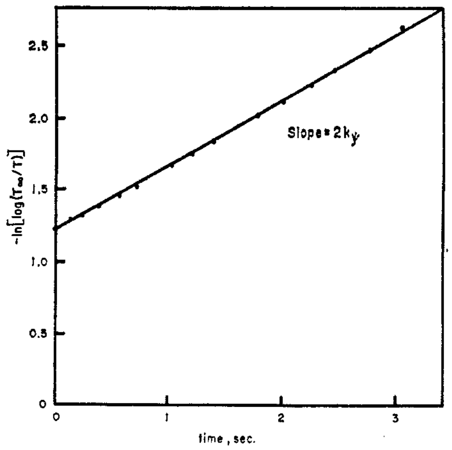

Figure 1—A typical kinetic plot.

TABLE II

KINETIC DEPENDENCE ON IONIC STRENGTH

([cyclohexanenitronate anion] = 4.0 × $10^{-3}$ *M*, [MnO$_4^-$] = 4.00 × $10^{-4}$ *M*, pH 13.0, *T* = 1.0 ± 0.02°, λ 522 mμ)

| $\mu$ | $2k_\psi$ × $10^2$ sec$^{-1}$ |
|---|---|
| 0.10 | 78 ± 2 |
| 0.30 | 102 ± 4 |
| 0.50[a] | 122 |
| 0.75 | 148 ± 4 |
| 1.0 | 159 ± 1 |

[a] One determination.

TABLE III

KINETIC RESULTS FOR THE OXIDATION OF CYCLOPENTANENITRONATE ANION

($\mu$ = 0.5 *M*, λ 522 mμ, *T* = 1.0 ± 0.02°, 10-mm cell)

| [Cyclopentanenitronate anion] × $10^4$ *M* | [OH$^-$], *M* | [MnO$_4^-$] × $10^4$ *M* | $2k_\psi$ × $10^2$ sec$^{-1}$ | $2k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|
| 20.0 | 0.10 | 4.00 | 12.3 ± 0.2 | 61.4 |
| 40.0 | 0.10 | 4.00 | 23.2 ± 0.2 | 58.1 |
| 55.6 | 0.10 | 4.00 | 32.7 ± 0.4 | 58.8 |
| 80.0 | 0.10 | 4.00 | 45.6 ± 1 | 57.1 |
| 100.0 | 0.10 | 4.00 | 54.5 ± 3 | 54.5 |
| 40.0 | 0.01 | 4.00 | 21.7 ± 0.2 | 54.2 |
| 40.0 | 0.032 | 4.00 | 24.2 ± 0.2 | 60.0 |
| 40.0 | 0.10 | 4.00 | 23.2 ± 0.2 | 58.1 |
| 40.0 | 0.32 | 4.00 | 24.2 ± 0.4 | 60.5 |
| 116.5[a] | 0.10 | 4.00 | 45.1 ± 0.6 | 38.7 |
| 116.5[a] | 0.10 | 6.00 | 48.8 ± 0.3 | 41.9 |
| 116.5[a] | 0.10 | 8.00 | 49.9 ± 2 | 42.8 |
| 116.5[a] | 0.10 | 10.00 | 48.9 ± 0.2 | 41.9 |
| 116.5[a] | 0.10 | 12.00 | 49.3 ± 1 | 42.3 |

[a] 4-mm cell.

**Cyclopentanenitronate Anion (II).**—Table III summarizes the kinetic results for the oxidation of II. It is seen that $k_2$ is constant over a fivefold range of II concentration, and a plot of $k_\psi$ *vs.* II gives a straight line that goes through the origin which indicates a first-order dependence on II. That the rate of oxidation is independent of pH is demonstrated by the constancy of $k_2$ over a 32-fold range of hydroxide ion concentration. A change in permanganate concentration over a fivefold range, at constant concentrations of II and hydroxide ion, does not alter $k_\psi$, which indicates a first-order dependence on permanganate. The rate law is the same as the one for I.

$$\frac{-\mathrm{d}[\mathrm{MnO_4}^-]}{\mathrm{d}t} = 2k_2[\text{cyclopentanenitronate anion}][\mathrm{MnO_4}^-]$$

**Activation Parameters.**—Table IV gives the thermodynamic data for the oxidation of I and II.

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[14] Although the Debye–Hückel theory applies quantitatively only in dilute solutions, it can still be used to predict qualitatively the direction in which ionic strength influences reaction rates.

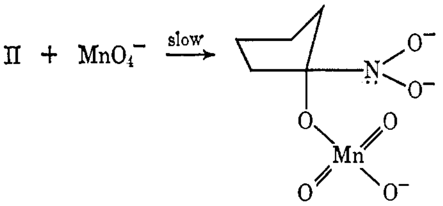
TABLE IV

ACTIVATION PARAMETERS FOR THE PERMANGANATE OXIDATION OF NITRONATE ANIONS

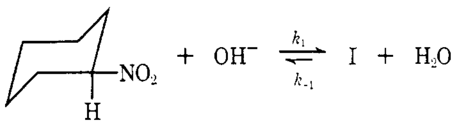
| Substrate | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu |
|---|---|---|
| I | 7.45 | −27.8 |
| II | 10.5 | −20.0 |

## Discussion

In basic solution nitrocycloalkanes form relatively stable nitronate anions[10–13] with unsaturated systems which are particularly vulnerable to nucleophilic attack.[15] The kinetic data suggest a scheme in which the nitronate anion is formed in an equilibrium step ($k_1 >>> k_{-1}$) and is oxidized by permanganate in the rate-determining step. A reasonable mechanism conforming to the observed kinetics would be[16,17] that given by reactions 2–5. The slow step (eq 3) is an attack of permanganate at the trigonal carbon of I or II to give the activated complex V or VII. This requires a change in rehybridization from sp$^2$ to sp$^3$ which predicts that II should react at a slower rate than I since the activated complex VII would be more strained (*I* strain[17–19]) than V. While there is considerable decrease in angular deformation in going from II to VII, the increased torsional strain in VII more than outweighs it, and the rate is decreased.

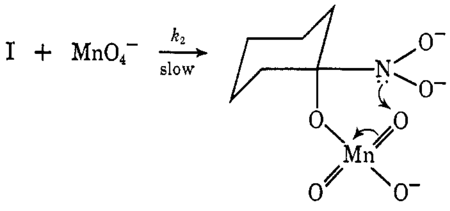


VII



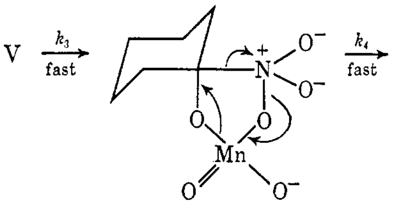
III

(2)

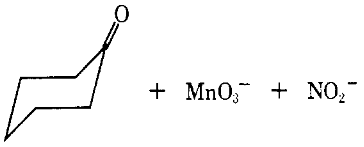


V

(3)



VI



(4)

$$MnO_3^- + MnO_4^- + 2OH^- \xrightarrow[\text{fast}]{k_5} 2MnO_4^{2-} + H_2O \quad (5)$$

An attempt to demonstrate this mechanism using permanganate $^{18}$O was inconclusive owing to the rapid exchange of both cyclohexanone[20] and permanganate[21,22] with solvent in the strongly alkaline media.

Although the observed kinetic data are in agreement with the mechanism presented, it gives no information on alternate reaction pathways for the activated complexes. Further data on the kinetics of the possible subsequent steps as well as information on the steric requirements of the cycloalkylnitronate anions are under investigation.

**Registry No.**—I, 12349-47-2; II, 12349-48-3.

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[15] I assumes the chair conformation and II probably assumes the *half-chair* conformation. See also F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

[16] Alternatively, a *cis* cycloaddition of permanganate to I could give VI directly. However, the $\Delta S^{\ddagger}$ values, which are no doubt controlled largely by solvation effects, are not sufficiently negative to require a cyclic transition state. The significance of the magnitude of $\Delta S^{\ddagger}$ is further complicated by the fact that a vast majority of permanganate oxidations have large negative entropies of activation.

[17] Hypomanganate ($MnO_3^-$) is instantaneously oxidized by permanganate to manganate ion ($MnO_4^{2-}$) which slowly disproportionates to permanganate and manganese dioxide under the reaction conditions: F. R. Duke, *J. Phys. Chem.*, **56**, 882 (1952).

[18] H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951); H. C. Brown, *Rev. Chem. Progr.*, **14**, 83 (1953).

[19] The concept of *I* strain has been modified in recent times to include all strains from compression of van der Waals radii, bond opposition forces, and distortion of bond angles.

[20] K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 238.

[21] N. F. Hall and O. R. Alexander, *J. Amer. Chem. Soc.*, **62**, 3455 (1940).

[22] G. A. Mills, *ibid.*, **62**, 2833 (1940).