melted from 205 to 240° where some sublimation was noted. The mixture was dissolved in acetone and analyzed with a Hewlett-Packard Model 5750 gas chromatograph and Infotronics Digital Readout CRS-108 integrator using a 6 ft × 0.125 in. Carbowax 20M column at 180°. Six distinct peaks were obtained and the fifth peak had a definite shoulder indicating two components for that peak. The area percentages calculated for each peak appear in Table I.

Separation and Identification of Isomers.—The crude mixture from the Meisenheimer reaction was separated with a Hewlett-Packard Model 5750 gas chromatograph using a 20 ft × 0.375 in. o.d. aluminum column filled with 20% Carbowax 20M on Chromosorb W. The sample was dissolved in acetone and injected into the column at 230°. The components of the six individual peaks were collected and the two components of peak 5 were separated by fractional sublimation. The components were identified by their mass, infrared, and nmr spectra and by comparison with spectra of synthetic isomers where possible. Mixture melting points were used in three cases as additional proof of structure. In the cases where infrared and nmr spectra of synthetic isomers and separated isomers could be obtained, they were identical in all respects leaving no doubt as to the identity of the compound. The melting point of 3,8-dichloro-1,5-naphthyridine separated from the mixture was 177.5–178.5° and the mixture melting point with the synthetic sample occurred at 177–178.5°. The melting point of separated 2,4-dichloro-1,5-naphthyridine from peak 5 was 124.5–130°. The melting point of separated 2,6-dichloro-1,5-naphthyridine from peak 5 was 257–260° and the mixture melting point with synthetic 2,6-dichloro-1,5-naphthyridine occurred at 257–259°. The melting point of 2,8-dichloro-1,5-naphthyridine, separated as peak 6 from the Meisenheimer mixture, was 154.5–156° and the mixture melting point with synthetic 2,8-dichloro-1,5-naphthyridine occurred at 154–157°. All of these melting points in this section were taken in a sealed tube and are uncorrected.

Registry No.—**2,** 27017-66-9; **3,** 28252-73-5; **4,** 28252-74-6; **5,** 28252-75-7; **6,** 28252-76-8; **7,** 28252-77-9; **8,** 28252-78-0; **9,** 28252-79-1; **10,** 28312-61-0; **11,** 28252-80-4; 3,8-dichloro-1,5-naphthyridine, 28252-81-5; 2,4-dichloro-1,5-naphthyridine, 28252-82-6; 2-chloro-1,5-naphthyridine, 7689-62-5; 4-chloro-1,5-naphthyridine, 7689-63-6; 2,7-dichloro-1,5-naphthyridine, 28252-85-9.

Permanganate Ion Oxidations. VI. Kinetics and Mechanism of the Oxidation of Alkanenitronate Anions[1]

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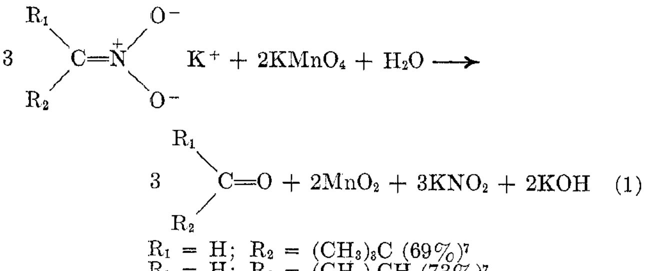
The kinetics of the permanganate ion oxidation of the alkanenitronate anions from nitromethane, nitroethane, 1- and 2-nitropropane, and 1- and 2-nitrobutane have been studied by spectrophotometric stopped-flow techniques. Between pH 11.6 and 13.7 the reaction follows the rate law $\nu = k[\text{alkanenitronate anion}][\text{MnO}_4^-]$. The reactions are characterized by low enthalpies of activation ($\Delta H^{\ddagger} = 6.00$ to 8.84 kcal/mol) and large negative entropies of activation ($\Delta S^{\ddagger} = -16.0$ to -23.0 eu). A positive salt effect is observed, and correlation of σ^* substituent values and second-order rate constants gives a ρ of 0.53 at 10°. The kinetic data suggest that the rate-determining step involves a stepwise addition of permanganate ion to the carbon of the carbon–nitrogen double bond in the alkanenitronate anion. Possible activated complexes for the permanganate ion oxidation of cyclohexanenitronate anion and phenylmethanenitronate anions are also discussed.

Although kinetic and mechanistic studies of the alkaline permanganate ion oxidation of the potassium salts of phenylmethanenitronate anions,[2,3] cyclopentanenitronate anion,[4] and cyclohexanenitronate anion[4] have been reported in recent years, not one of them has been concerned with the permanganate ion oxidation of simple alkanenitronate anions.[5] The permanganate ion oxidation of the potassium salts of aliphatic nitro compounds is an excellent preparative method[6,7] for the synthesis of aldehydes and ketones (eq 1).[6–10] These reactions are also of interest because of their extremely rapid rates of oxidation (k_2 larger than 100 l. mol^{-1} sec^{-1}). It is the purpose of this work to point out some pertinent features of a reasonable mechanism proposed herein for the permanganate ion oxidation of alkanenitronate anions.



$$3\,R_1R_2C{=}\overset{+}{N}(O^-)_2\ K^+ + 2KMnO_4 + H_2O \longrightarrow 3\,R_1R_2C{=}O + 2MnO_2 + 3KNO_2 + 2KOH \quad (1)$$

$R_1 = H$; $R_2 = (CH_3)_3C$ (69%)[7]
$R_1 = H$; $R_2 = (CH_3)_2CH$ (73%)[7]
$R_1 = H$; $R_2 = CH_3(CH_2)_2$ (97%)[7]
$R_1 = CH_3$; $R_2 = (CH_3)_3C$ (94%)[7]
$R_1 = R_2 = CH_3$ (96%)[7]

Experimental Section

Reagents.—2-Nitropropane,[11,12] 1-nitropropane,[12] 1-nitrobutane,[13,14] 2-nitrobutane,[13,14] nitromethane,[12] and nitroethane[11] were distilled immediately before use. Distilled water, which was passed through an ion-exchange cartridge (Type R-2, Illinois Water Treatment Co., Rockford, Ill.), was used to prepare all solutions. Potassium chloride (Malinckrodt) was used to maintain 1.0 *M* ionic strength. Potassium permanganate stock solutions were prepared from Acculute standard volumetric concentrates. The pH, which was measured potentiometrically, was adjusted with Acculute standard volumetric potassium hydroxide (CO_2 free) concentrate.

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[1] Previous paper in series: F. Freeman and M. A. H. Scott, *J. Org. Chem.*, **35**, 2989 (1970).

[2] F. Freeman and A. Yeramyan, *Tetrahedron Lett.*, 4783 (1968).

[3] F. Freeman and A. Yeramyan, *J. Org. Chem.*, **35**, 2061 (1970).

[4] F. Freeman, A. Yeramyan, and F. Young, *ibid.*, **34**, 2438 (1969).

[5] H. B. Hass and M. L. Bender [*J. Amer. Chem. Soc.*, **71**, 1767 (1949)] have suggested that alkali salts of nitroalkanes be named as metal alkanenitronates.

[6] H. Shechter and R. B. Kaplan, *ibid.*, **75**, 3980 (1953).

[7] H. Shechter and F. T. Williams, Jr., *J. Org. Chem.*, **27**, 3699 (1962).

[8] S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **47**, 1590 (1915).

[9] S. Nametkin and O. Madaeff-Ssitscheff, *Chem. Ber.*, **52**, 370 (1926).

[10] S. Nametkin and A. Zabrodina, *ibid.*, **69**, 1789 (1936).

[11] Commercial Solvents Corp.

[12] Aldrich Chemical Co., Inc.

[13] Sample from Professor H. Feuer, Department of Chemistry, Purdue University, Lafayette, Ind.

[14] Sample from Dr. A. T. Nielsen, U. S. Naval Ordnance Test Station, China Lake, Calif.

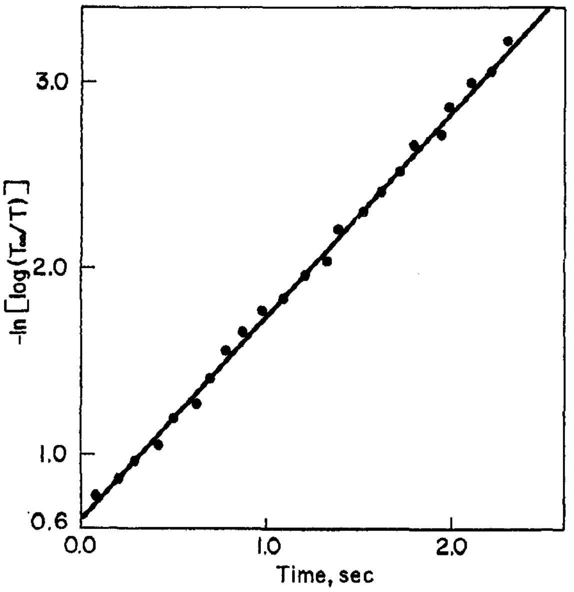

Figure 1.—A typical pseudo-first-order plot. The conditions are [2-propanenitronate anion] = 8×10^{-3} M, [OH^-] = 0.20 M, [MnO_4^-] = 4.0×10^{-4} M, μ = 1.0, λ = 510 mμ, T = 0.0°.

Rate Procedures.—The rates were determined by observing the disappearance of permanganate ion at 510 and 522 mμ, and the rate constant determinations were made using a specially designed stopped-flow reactor.[3,4] Pseudo-first-order rate constants (k_ψ) were calculated from the slopes of plots of $-\ln[\log(T_\infty/T)]$ against time (Figure 1) on a CDC 3300 computer.[15,16] The rate constants given in the tables are the average of two or more determinations.

Temperature in the stopped-flow cell was maintained (±0.02°) with a Forma Model 2095-2 refrigerated and heated bath and circulator. Dry air was blown around the cell to preclude condensation at low temperatures.

Results

Kinetic Data.—The kinetic data for the permanganate ion oxidation of 2-propanenitronate anion (1) are summarized in Table I. The first-order dependence on the concentration of 1 is shown in the plot (Figure 2) of the pseudo-first-order rate constant (k_ψ) *vs.* an eightfold range of concentration of 1 which gives a straight line that goes through the origin. The constancy of the pseudo-first-order rate constant (k_ψ) at constant hydroxide ion and 1 concentrations and changing permanganate ion concentration indicates a first-order dependence on permanganate ion. Figure 1, which illustrates a typical linear pseudo-first-order plot, further confirms the first-order dependence on permanganate ion concentration. The effect of hydroxide ion concentration on the rate of oxidation is summarized in Table II.

TABLE I

PERMANGANATE ION OXIDATION OF 2-PROPANENITRONATE ANION AT pH 13.0[a]

[2-Propanenitronate anion], 10^3 M	[MnO_4^-] × 10^4 M	k_ψ,[b] sec^{-1}	k_2[c] × 10^{-2} M^{-1} sec^{-1}
2.0	4.0	0.297	1.48
4.0	4.0	0.606	1.51
6.0	4.0	0.867	1.45
8.0	4.0	1.18	1.48
12.0[d]	4.0	1.71	1.42
16.0[e]	4.0	2.14	1.33
8.0	2.0	0.991	1.24
8.0	6.0	1.10	1.37
8.0	8.0	1.14	1.42
8.0[f]	2.0	0.955	1.24
8.0[f]	4.0	1.12	1.40
8.0[f]	6.0	0.993	1.24
8.0[f]	8.0	1.05	1.33

[a] [OH^-] = 0.1 M, μ = 1.0, λ = 510 mμ, T = 0.0°. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[2-propanenitronate anion]. [d] One determination. [e] Rate almost too fast for the capability of the stopped-flow system. [f] λ = 522 mμ.

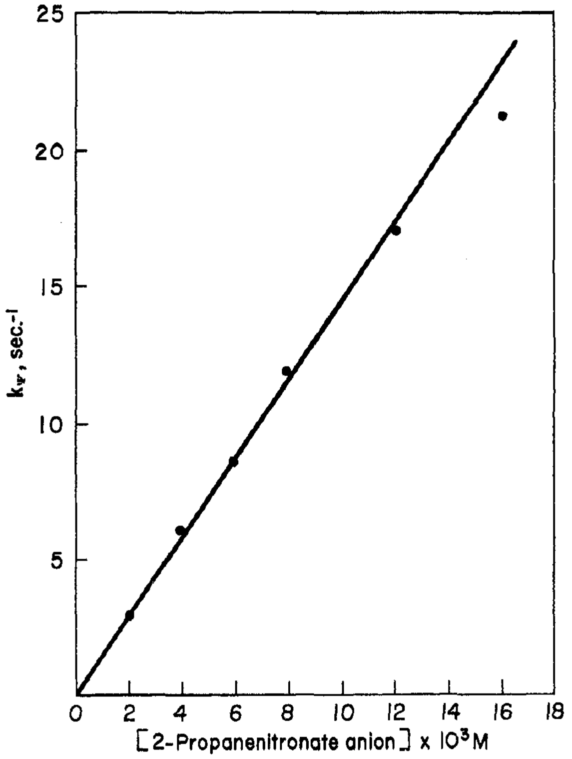

Figure 2.—Effect of potassium 2-propanenitronate on the pseudo-first-order rate constants for the permanganate ion oxidation of potassium 2-propanenitronate at 0.0°.

TABLE II

KINETIC DEPENDENCE ON HYDROXIDE ION CONCENTRATION[a]

[OH^-], M	pH	k_ψ,[b] sec^{-1}
1.4×10^{-5}	9.14[c]	0.64
1.3×10^{-3}	11.1[c]	0.86
3.9×10^{-3}	11.6[c]	0.93
0.02	12.3	0.95
0.085	12.9	0.90
0.10	13.0	1.14
0.17	13.2	1.00
0.32	13.5	1.00
0.50	13.7	1.14

[a] [2-Propanenitronate anion] = 8.0×10^{-3} M, [MnO_4^-] = 4.0×10^{-4} M, μ = 1.0, λ = 510 mμ, T = 0.0°. [b] Pseudo-first-order rate constant. [c] Unbuffered solution.

It is seen at constant 1 concentration and constant permanganate ion concentration that the pseudo-first-order rate constant (k_ψ) does not change appreciably on a 125-fold range of hydroxyl ion concentration; this observation confirms a zero-order dependence

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

[16] K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, p 168.

on hydroxide ion concentration. Consequently, the data are consistent with the following rate law.

$$\nu = k[\text{2-propanenitronate anion}][\mathrm{MnO_4^-}] \quad (2)$$

Effect of Added Salts on Rates.—Table III shows that there is a positive salt effect in the permanganate ion oxidation of **1**.

TABLE III

EFFECT OF IONIC STRENGTH ON THE RATE OF OXIDATION OF 2-PROPANENITRONATE ANION AT pH 13.0[a]

μ	k_ψ,[b] sec^{-1}	k_2,[c] M^{-1} sec^{-1}
0.1	0.46	57.3
0.25	0.63	79.4
0.50	0.81	101.6
0.75	0.95	118.6
1.0	1.09	136.0

[a] [2-Propanenitronate anion] = 8.0×10^{-3} M, [OH$^-$] = 0.1 M, [MnO$_4^-$] = 4.0×10^{-4} M, λ = 510 mμ, T = 0.0°. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[2-propanenitronate anion].

Thermodynamic Parameters.—The activation parameters for the permanganate ion oxidation of eight alkanenitronate anions are summarized in Table IV.

TABLE IV

ACTIVATION PARAMETERS FOR THE PERMANGANATE ION OXIDATION OF SOME ALKANENITRONATE ANIONS AT pH 13.0[a]

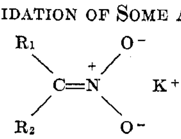
Anion	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
Methanenitronate[b]	13.1	8.51	16.6
Ethanenitronate[b]	13.0	8.40	16.4
1-Propanenitronate[b]	12.9	6.00	24.7
2-Propanenitronate[b]	13.3	8.84	16.0
1-Butanenitronate[b]	13.0	7.72	18.9
2-Butanenitronate[b]	13.3	6.86	23.0
Cyclohexanenitronate[c]	12.9	7.47	19.6
Phenylmethanenitronate[d,e]	13.1	6.58	23.5

[a] Calculated on a CDC 3300 computer. [b] This work. [c] Reference 4. [d] References 2 and 3. [e] pH 13.6.

Linear Free-Energy Relationships.—Table V summarizes the rate data for the permanganate ion oxidation of six alkanenitronate anions. Correlation of σ^* substituent constants and second-order rate constants (k_2) (excluding the value for methanenitronate anion) gives a ρ of 0.53, a correlation coefficient (r) of 0.963, and a standard deviation (s) of 0.045.

TABLE V

EFFECT OF SUBSTITUENTS ON THE RATE OF PERMANGANATE ION OXIDATION OF SOME ALKANENITRONATE ANIONS AT pH 13.3[a]

	k_ψ,[b] sec^{-1}	k_2,[c] M^{-1} sec^{-1}	$\Sigma\sigma^*$ [d]	Log k_2
$R_1 = R_2 = H$	1.47	368	0.980	2.57
$R_1 = H; R_2 = CH_3$	1.98	496	0.490	2.70
$R_1 = H; R_2 = CH_2CH_3$	2.19	548	0.390	2.74
$R_1 = H; R_2 = CH_2CH_2CH_3$	1.96	490	0.375	2.69
$R_1 = R_2 = CH_3$	1.12	280	0.000	2.45
$R_1 = CH_3; R_2 = CH_2CH_3$	1.11	277	−0.100	2.44

[a] [MnO$_4^-$] = 4.0×10^{-4} M, [OH$^-$] = 0.20 M, μ = 1.0, λ = 510 mμ, T = 10.0°. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[alkanenitronate anion]. [d] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

TABLE VI

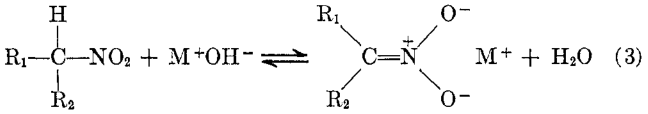
ACIDITY CONSTANTS OF SOME NITROALKANES

Nitroalkane	K_a	pK_a
Nitromethane[a,b]	6.1×10^{-11}	10.2
Nitroethane[a,b]	2.5×10^{-9}	8.6
1-Nitropropane[a,b]	1.1×10^{-9}	8.98
2-Nitropropane[b,c]	2.1×10^{-8}	7.7
1-Nitrobutane[c]	2.5×10^{-9}	8.6
2-Nitrobutane[c]	1.8×10^{-8}	7.8
Phenylnitromethane[c]	1.6×10^{-7}	6.8

[a] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **72**, 3574 (1950). [b] G. W. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943). [c] W. Kemula and W. Turnowska-Rubaszewska, *Rocz. Chem.*, **37**, 1597 (1963).

Discussion

Primary and secondary nitroalkanes yield alkali metal salts in sodium or potassium hydroxide solution (Table VI). Self-consistent molecular orbital calculations[17,18] and ultraviolet,[18] infrared,[19] and Raman[19] spectra suggest that in alkanenitronate anions there is a delocalization of the six π electrons which results in essentially a C=N and two equivalent N—O bonds with low double bond character.



$$R_1C(H)(R_2)NO_2 + M^+OH^- \rightleftharpoons R_1R_2C{=}\overset{+}{N}(O^-)_2 \quad M^+ + H_2O \quad (3)$$

$R_1 = H$; $R_2 =$ alkyl
$R_1 = R_2 =$ alkyl
$M^+ =$ potassium or sodium

It is seen from the kinetic data that the permanganate ion oxidation of alkanenitronate anions is zero order in hydroxide ion concentration, first order in alkanenitronate anion concentration, and first order in permanganate ion concentration. The zero-order dependence on hydroxyl ion concentration is consistent with a mechanism involving the alkanenitronate anion and permanganate ion in the rate-controlling step (Scheme I). Although Scheme I depicts the formation of **4** as the slow step, the kinetic data do not exclude the formation of **5**, *via* a concerted cis cycloaddition, as the rate-limiting step (eq 4).

$$\mathbf{3} + \mathrm{MnO_4^-} \xrightarrow{\text{slow}} \mathbf{5} \quad (4)$$

The data on the effect of alkyl substituents (Table V) show that an increase in alkyl substitution on the carbon of the C=N causes only a slight change in the rate of oxidation. The observed small ρ value (0.53) is similar to the small values obtained in the permanganate ion oxidation of phenylmethanenitronate anions (−0.67),[3] in the permanganate ion oxidation of salts of unsaturated carboxylate anions ($\cong$0),[15] and in cis-1,3-dipolar cycloaddition reactions (+0.8 to +1.2).[20] Consequently, the activated complex in the permanganate ion oxidation of alkanenitronate

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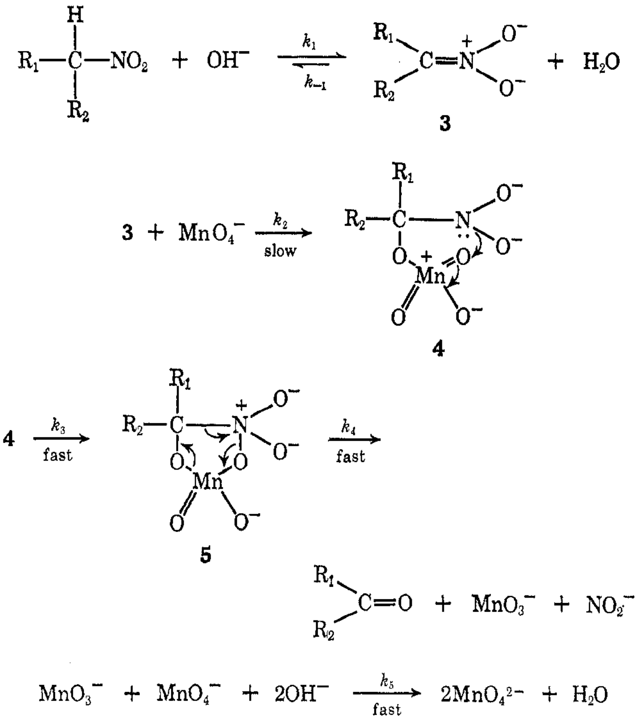
(17) N. Jonathan, *J. Mol. Spectrosc.*, **7**, 105 (1961).

(18) F. T. Williams, Jr., P. W. K. Flanagan, W. G. Taylor, and H. Shechter, *J. Org. Chem.*, **30**, 2674 (1965).

(19) M. J. Brookes and N. Jonathan, *Spectrochim. Acta, Part A*, **25**, 187 (1969).

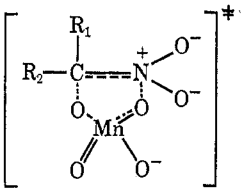
(20) R. Huisgen, R. Graskey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 844.

SCHEME I



anions probably has a close resemblance to either structure **4** or **5**.

1,3-Dipolar cycloaddition reactions require strict orientation of the components in the activated complex. Consequently these reactions are characterized by small values for the enthalpy of activation and large negative values for the entropies of activation ($\Delta S^{\ddagger} = -25$ to -45 eu). Permanganate ion presumably reacts with unsaturated systems *via* a concerted cis-cycloaddition mechanism.[3,15,21,22] These oxidations have $\Delta H^{\ddagger}$ values of 4.8 to 7.5 kcal/mol and $\Delta S^{\ddagger}$ values of -24 to -36 eu.[15] It is seen that the observed $\Delta S^{\ddagger}$ values (-16.0 to -23.0 eu) for the permanganate ion oxidation of alkanenitronate anions are not very similar to cis-1,3-dipolar cycloadditions[23,24] and permanganate ion cycloaddition reactions. Therefore, the activated complex for the permanganate ion oxidation of alkanenitronate anions probably cannot have a very close resemblance to **6**.[25]



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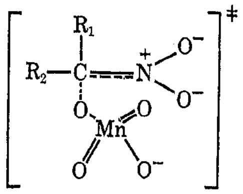
There is a remarkable similarity among the salt effects, $\Delta F^{\ddagger}$ values, $\Delta H^{\ddagger}$ values, and $\Delta S^{\ddagger}$ for the permanganate ion oxidation of alkanenitronate anions, cyclopentanenitronate anion,[4] cyclohexanenitronate anion,[4] phenylmethanenitronate anions,[2,3] and other anions.[2,26] Consequently the kinetic data for the permanganate ion oxidation of alkanenitronate anion, and probably for cycloalkylnitronate anions and phenylnitromethane nitronate anions, are consistent with a rate-determining attack of permanganate ion at the carbon of the C=N with a synchronous movement of a pair of electrons to the nitrogen atom to give the possible activated complex (**7**). Carbon–oxygen bond formation logically leads to the intermediate **4** which then rearranges to **5** according to Scheme I.



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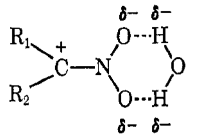
The argument against activated complex **6**, which is partly based on $\Delta S^{\ddagger}$ values, is an oversimplification[25] since the charge type of the reactants for the alkanenitronate anion oxidation is not the same as the model reactants. Also, values of $\Delta S^{\ddagger}$ are known to be determined by solvation effects in many reactions,[4] and a vast majority of permanganate ion oxidations generally have large negative entropies of activation.[1-4,15,26] Consequently, one must also consider structures such as **8–11**, which influence the charge density at the nitronate carbon and the carbon–nitrogen double bond character, in a discussion of the influence of electronic, steric, and solvation factors on the mechanism.[4,27]



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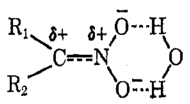

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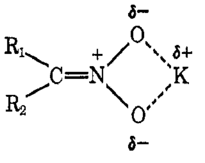

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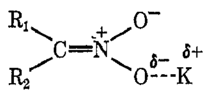

11

Registry No.—Potassium methanenitronate, 28273-52-1; potassium ethanenitronate, 26241-08-7; potassium 1-propanenitronate, 28273-54-3; potassium 2-propanenitronate, 28273-55-4; potassium 1-butanenitronate, 28273-56-5; potassium 2-butanenitronate, 28273-57-6.

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

[22] V. Boeseken, *Recl. Trav. Chim. Pays-Bas*, **40**, 553 (1921).

[23] Reference 20, p 834.

[24] R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).

[25] Although bond formation begins simultaneously, cycloaddition does not require that the two new bonds be formed at identical rates. Bond formation at different rates could lead to charge separation in the transition state region.

[26] F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. G. McLaughlin, and E. W. Paull, *J. Org. Chem.*, **35**, 982 (1970); S. M. Taylor and J. Halpern, *J. Amer. Chem. Soc.*, **81**, 2933 (1959).

[27] M. Fukujama, P. W. K. Flanagan, F. T. Williams, Jr., L. Frainier, S. A. Miller, and H. Shechter, *ibid.*, **92**, 4689 (1970).