Glycidyltrimethylammonium Bromide.—A solution of 15 g (0.25 mol) of trimethylamine and 29 g (0.21 mol) of epibromohydrin in 70 ml of dimethoxyethane was stirred at 0-20° for 18 hr. External cooling was necessary to maintain the temperature. The white crystals were collected by filtration and washed with ether in a drybox. After drying *in vacuo* at 35°, the halide weighed 38 g (92% yield), melted at 151-153°, and had an epoxide value of 0.50 equiv/100 g (98% of theory).

Registry No.—I, 3033-77-0; glycidyltriethylammonium chloride, 15876-88-7; glycidyltrimethylammonium bromide, 13895-77-7.

The Nature of the Activated Complex in the Permanganate Oxidation of Phenylmethanenitronate Anions[1,2]

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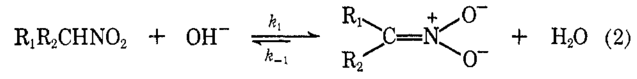
Received November 3, 1969

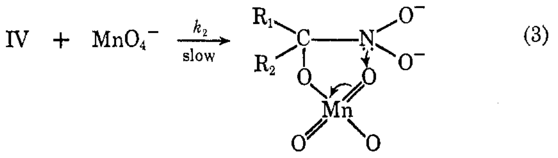
The neutral or alkaline permanganate oxidation of nitronate anions has been shown to give excellent yields of aldehydes and ketones.[3,4] Kinetic studies in our laboratories of phenylmethanenitronate anion (I),[5] cyclohexanenitronate anion (II), and cyclopentanenitronate anion (III)[6] have shown in strongly alkaline media[7] that the reaction is zero order in hydroxide ion, first order in permanganate ion, and first order in nitronate anion. The $\Delta H^{\ddagger}$ for the oxidation of I is 7.5 kcal/mol and $\Delta S^{\ddagger}$ is -20 eu.[5] The entropy of activation for the oxidation of II and III are -20 and -27.8 eu, respectively.[6] It was proposed that the rate-determining step involves an attack of permanganate at the carbon of the carbon–nitrogen double bond of the nitronate anion[11] to give V, which rearranges to the observed products according to eq 4.[5,6]

$$3R_1R_2C{=}NO_2K + 2KMnO_4 + H_2O \longrightarrow 3R_1R_2C{=}O + 2MnO_2 + 3KNO_2 + 2KOH \quad (1)$$



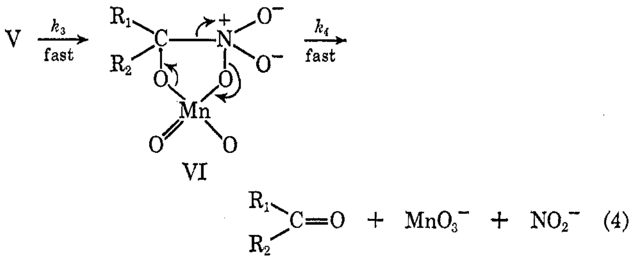
$$R_1R_2CHNO_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_1R_2C{=}\overset{+}{N}(O^-)O^- + H_2O \quad (2)$$

IV



(3)

V



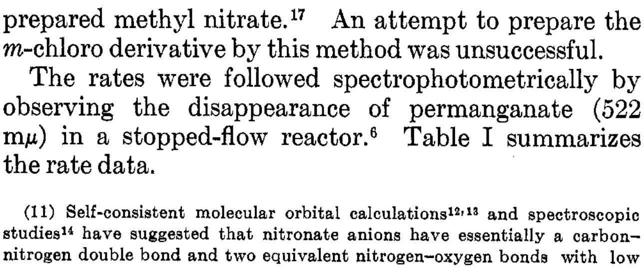
VI

(4)

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

Support for the postulated slow step, which involves a change in hybridization from sp^2 to sp^3 at the carbon of the C=N, was obtained from the observation that II reacted six times as fast as III.[1,15] However, the kinetic data are not inconsistent with the formation of VI, *via* the typical permanganate *cis*-cycloaddition mechanism, as the rate-determining step (eq 4). In the hope that the effect of substituents might reveal something about the nature of the activated complex in the rate-limiting step of the permanganate oxidation of I, we investigated the rates of oxidation of several nitronate anions derived from the corresponding *para*-substituted phenylnitromethanes.

Phenyl-, *p*-bromophenyl-, and *p*-methylphenylnitromethane were prepared by treating the respective benzyl bromides with freshly prepared silver nitrite.[16] However, the *m*-methyl derivative appeared to decompose during distillation. *p*-Chlorophenyl-, *p*-nitrophenyl-, and *p*-methoxyphenylnitromethane were prepared by treating their respective cyanides with freshly prepared methyl nitrate.[17] An attempt to prepare the *m*-chloro derivative by this method was unsuccessful.



(6)

The rates were followed spectrophotometrically by observing the disappearance of permanganate (522 mμ) in a stopped-flow reactor.[6] Table I summarizes the rate data.

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[1] Previous paper in series: F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. G. McLaughlin, and E. W. Paull, *J. Org. Chem.*, in press.

[2] Abstracted in part from the M.S. thesis of A. Yeramyan, California State College, Long Beach, Calif., 1969.

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

[4] S. S. Nametkin and O. Madaeff-ssitscheff, *Chem. Ber.*, **59**, 370 (1926).

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

[6] F. Freeman, A. Yeramyan, and F. Young, *J. Org. Chem.*, **34**, 2438 (1969).

[7] Kinetic studies were performed between pH 12.5 and 13.6. At the higher pH values, phenylnitromethane[8,9] and the nitrocycloalkanes[9,10] are essentially completely converted into the nitronate anions.

[8] W. Kemula and W. Turnowska-Rubaszewska, *Rocz. Chem.*, **37**, 1597 (1963).

[9] F. Freeman and A. Yeramyan, unpublished data, 1969.

[10] P. W. K. Flanagan, H. W. Amburn, H. W. Stone, J. G. Trayham, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969).

[11] Self-consistent molecular orbital calculations[12,13] and spectroscopic studies[14] have suggested that nitronate anions have essentially a carbon–nitrogen double bond and two equivalent nitrogen–oxygen bonds with low double-bond character.

[12] N. Jonathan, *J. Mol. Spectrosc.*, **7**, 105 (1961).

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

[14] M. J. Brookes and N. Jonathan, *Spectrochim. Acta*, **25A**, 187 (1969).

[15] III presumably reacts at a slower rate as a result of the increase of I strain (bond opposition forces, compression of van der Waals radii, and distortion of bond angles) in going from IV to V: H. C. Brown and M. Bordowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952).

[16] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *ibid.*, **77**, 6269 (1955).

[17] A. P. Black and F. H. Babers in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1943, pp 412, 512.

TABLE I

EFFECT OF SUBSTITUENTS ON THE RATE OF OXIDATION AT 1°
($[MnO_4^-] = 4.0 \times 10^{-4}M$, pH = 13.6, $\mu = 0.5$, $\lambda = 522$ mμ)

Substituent	$[R_1R_2C{=}NO_2^-]$ $\times 10^3$ M	k_ψ,[a] sec^{-1}	k_2,[b] M^{-1} sec^{-1}
p-OCH_3	5.01	2.04	405.6
p-CH_3	5.03	1.16	230.6
H	5.00	0.65	130.0
p-Cl	5.00	0.60	120.0
p-Br	5.01	0.44	87.8

[a] Pseudo-first-order rate constant. [b] Second-order rate constant $= k_\psi/[R_1R_2C{=}NO_2^-]$.

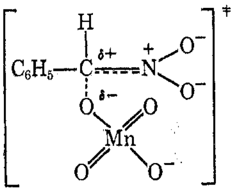
TABLE II

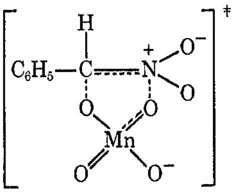
PREPARATION AND PHYSICAL PROPERTIES OF PHENYLNITROMETHANE DERIVATIVES

Phenylnitromethane derivative	Method of preparation	Mp or bp (mm), °C	Lit. mp or bp (mm), °C	$n^{20}D$	Lit. $n^{20}D$
p-H	A[a,b]	68–71 (0.5)	77–79 (1)[c]	1.5322	1.5315[c]
p-Br	A[a]	51.0–51.5	50[d]		
p-CH_3	A[a]	99–102 (3)	99 (3)[e]	1.5281	1.5278[e]
m-CH_3[f]	A[a]				
p-Cl	B[g,h]	29.5–30.0	33[i]		
m-Cl[j]	B[g]				
p-OCH_3	B[g]	135–138 (2)	106–108 (6)[a,k]	1.5460	1.5400[a]
p-NO_2[l]	B[g]	88.5–89.0	91–92[e]		

[a] Reference 16. [b] Corresponding benzyl bromide and silver nitrite. [c] Reference 21. [d] Reference 22. [e] Reference 23. [f] Product decomposed during distillation. [g] Reference 17. [h] Corresponding benzyl cyanide and methyl nitrate. [i] Reference 24. [j] No product was obtained in one experiment.[9] [k] Reference 25. [l] Basic solution gave an orange color.

Correlation of σ^+ substituent and rate constants (log k_2) gives a ρ^+ of -0.67 with a correlation coefficient (r) of 0.984 and a standard deviation (s) of 0.0546. The magnitude of the reaction constant, although small, is consistent with the formation of a small or negligible positive charge at the benzylic carbon of I. Similar small ρ values have been obtained for the permanganate oxidation of alkenyl anions ($\rho \cong 0$)[18] and for *cis*-1,3-dipolar cycloaddition reactions ($\rho = +0.8$).[19] Consequently, the rate data are consistent with an activated complex which involves partial bonding of permanganate with one or both termini of the carbon–nitrogen double bond[11] with little or no development of positive charge at the benzylic carbon. The partly bridged resonance-stabilized activated complex (VII) or the cyclic manganese (V) ester activated complex (VIII) is entirely consistent with the kinetic data.[20] This also implies that the rate-determining step could be eq 3 or 4.[20] However, the entropy of activation (−20 eu), which is smaller than those observed for the permanganate oxidation of alkenyl anions (−27 to −36 eu),[18] is similar to the values for the oxidation of other anions,[1,6] and is more consistent with the formulation of VII as the activated complex. The entropy of activation for *cis*-1,3-dipolar cycloadditions are also generally large and negative (−27 to −49 eu).[19]


VII


VIII

Experimental Section

All melting points are uncorrected and were determined on a Thomas–Hoover apparatus. Ultraviolet spectra were taken in a Beckman DK-2A spectrophotometer, and the kinetics were performed with a Beckman DU spectrophotometer and a Bristol strip–chart recorder.

Phenylnitromethane Derivatives.—The phenylnitromethanes used in this work were prepared by the methods indicated in Table II, which also lists physical properties and literature values.[21–25]

Reagents.—Distilled water was purified by passing through two type R-2 ion-exchange columns.[26] Standard volumetric (Acculute) potassium hydroxide (CO_2 free) concentrate was diluted to the specified volume for the desired pH. Potassium permanganate stock solutions were also prepared from standard volumetric solutions (Acculute). The stock solution was stored under nitrogen and the absorbancy index was checked before each set of kinetic runs. Reagent grade sodium chloride (Mallinckrodt) was used without further purification to adjust ionic strength. All solutions were prepared immediately before use, and the pH was measured potentiometrically.

Kinetic Method.—Because of the rapid rate of oxidation, the kinetics were determined by observing the disappearance of permanganate at 522 mμ, in a stopped-flow reactor.[1,6] All studies were performed under pseudo-first-order conditions. The pseudo-first-order rate constants (k_ψ) were obtained from the slopes of plots of $-\ln[\log(T_\infty/T)]$ *vs.* time and were calculated on an IBM 360 computer.[27,28] T_∞ is the per cent transmission, after at least three half-lives, at a point just before colloidal manganese dioxide begins to form. The rate constants are the average of two or more determinations.

Registry No.—IV (R_1 = CN; R_2 = p-$OCH_3C_6H_5$), 12413-22-8; IV (R_1 = CN; R_2 = p-ClC_6H_5), 12413-20-6; IV (R_1 = H; R_2 = p-$CH_3C_6H_5$), 12413-21-7; IV (R_1 = H; R_2 = C_6H_5), 12413-18-2; IV (R_1 = H; R_2 = p-BrC_6H_5), 12413-17-1.

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(18) K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, **88**, 5827 (1966).

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

(20) Although structures VII and VIII are two activated complexes which fit the results, other possible activated complexes can also be drawn.

(21) M. Konovalow, *Chem. Zentr.*, **70**, 1238 (1899).

(22) J. Wislicenus and B. Elvert, *Chem. Ber.*, **41**, 4129 (1908).

(23) J. S. F. Pode and W. A. Waters, *J. Chem. Soc.*, 717 (1956).

(24) J. von Raalte, *Rec. Trav. Chim. Pays-Bas*, **18**, 392 (1899).

(25) p-Methoxyphenylnitromethane has been reported as an orange or yellow liquid.[16] We observed that it is a colorless liquid which is unstable and becomes yellow during distillation and during storage at −60 to −70°.

(26) Illinois Water Treatment Co., Rockford, Ill.

(27) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, Inc., New York, N. Y., 1965, p 168 ff.

(28) We wish to thank the Western Data Computing Center, University of California, Los Angeles, Calif., for making computer time available to us.