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KINETICS OF THE PERMANGANATE OXIDATION OF PHENYLNITROMETHANE

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Most bimolecular organic reactions have rate constants under 1 l. mole^{-1} sec^{-1}. Wiberg and Geer[1] have reported unusually large second order rate constants, in excess of 100 l. mole^{-1} sec^{-1}, for the permanganate oxidation of acetone and alkenes. We wish to report that the permanganate oxidation of phenylnitromethane[2] (I) in basic media gives rate constants in excess[3] of 150 l. mole^{-1} sec^{-1}. Because of the short reaction times, the rates of reaction were determined spectrophotometrically via the disappearance of permanganate using a stopped-flow reactor[4] and a high speed strip-chart recorder.

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

Schechter and Williams[2] reported that permanganate oxidizes the potassium salt of I to benzaldehyde in 97% yield. Although permanganate oxidizes benzaldehyde rapidly in basic media[5,6], its reaction with the salt of I is much faster.[2,7] No kinetic data has been previously reported concerning the permanganate oxidation of nitro compounds.

The kinetic data for the oxidation of I at pH 13.6 and at 1.0±0.1°C are summarized in Table I. The constancy of the k_2 values at constant permanganate and hydroxyl ion concentrations indicates a first order dependence on phenylnitromethane concentration. A plot of k_2 versus the concentration of I gives a straight line passing through the origin, indicating a first order dependence on I. At constant permanganate and phenylnitromethane concentrations the rate constant does not change over seventeenfold range of base concentration, indicating a zero order dependence on hydroxyl ion concentration. To a first approximation, there is a first order

TABLE I

Permanganate Oxidation of Phenylnitromethane[a]

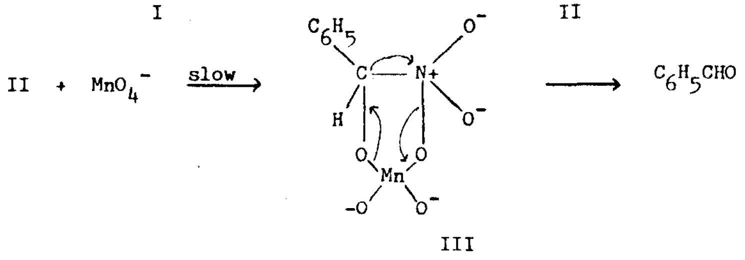
$[C_6H_5CH_2NO_2]$ x 10^3M	$[OH^-]$ x 10^2M	pH	$[MnO_4^-]$ x 10^4M	[c] k_ψ, 10^2 sec^{-1}	k_2, M^{-1} sec^{-1}
2.1	22.35	13.6	4.0	24.5±0.6	175.0
4.25	22.35	13.6	4.0	50.4±1.2	177.9
6.35	22.35	13.6	4.0	75.9±1.5	179.3
8.50	22.35	13.6	4.0	103.9±5.4	183.3
12.7	22.35	13.6	4.0	155.1±6.1	183.2
8.5	0.425	11.93	4.0	96.4±3.6	170.1
8.5	1.23	12.25	4.0	94.6±0.6	166.9
8.5	3.15	12.8	4.0	95.0±1.4	167.6
8.5	7.3	13.15	4.0	95.1±2.2	167.8
[b]6.35	22.35	13.6	6.0	86.7±4.0	204.8
[b]6.35	22.35	13.6	8.0	95.7±6.9	226.1
[b]6.35	22.35	13.6	10.0	95.0±6.0	224.4
[b]6.35	22.35	13.6	12.0	93.8±7.9	221.6
[b]6.35	22.35	13.6	14.0	90.0±17	212.6

[a] λ = 522 mμ, μ = 0.5M, Temp. = 1.0±0.1°C, 10 mm cell; [b] 4 mm cell;

[c] pseudo-first order rate constant, average of three runs.

$$C_6H_5CH_2NO_2 + KOH \rightleftarrows C_6H_5CH=NO_2K + H_2O \qquad (2)$$

I II



III

(3)

dependence on permanganate concentration at constant pH and constant phenylnitromethane concentration. This data suggests the following rate law:

$$\frac{-d\left[\mathrm{Mn}^{VII}\right]}{dt} = k\left[\mathrm{MnO_4^-}\right]\left[\mathrm{C_6H_5CH{=}NO_2^-}\right]$$

Hydroxide ion converts I to the nitronate ion[8] (II) which reacts with permanganate in the rate-determining step to form the Mn-V cyclic ester (III). Decomposition of III gives the observed products.

The low energy, 8.1±0.2 kcal/mole, the low enthalpy, 7.5±.2 kcal/mole and the large negative entropy, -20±1.0 e. u., of activation suggest a cyclic activated complex.[2,9] Also, the very large and negative $\Delta S^{\neq}$ is on the same order of magnitude as the $\Delta S^{\neq}$ values for anions with permanganate.[10,11] However, the thermodynamic parameters do not exclude other mechanistic possibilities.

We are investigating the effect of substitutents and other nitrocompounds in order to obtain more information about the nature of the activated complex.

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(3) Although larger rate constants are obtained under some experimental conditions, limitations in the stopped-flow system precluded further study. The rate of disappearance of permanganate is equal to 2/3 the rate of formation of benzaldehyde.

(4) Designed by Professor K. B. Wiberg, Department of Chemistry, Yale University.

(5) K. B. Wiberg and R. Stewart, *J. Am. Chem. Soc.*, **78**,1214 (1956).

(6) K. B. Wiberg and F. Freeman, 1965, unpublished data.

(7) The rate constant was calculated three times, using data to the first half-life, to the second half-life, and to the third half-life. The computer program compared this value with the theoretical points and any deviation from linearity was readily observed. All rate constants were calculated to at least 90% of reaction.

(8) Ultraviolet spectroscopy shows that I is completely converted to the ion by excess base under the reaction conditions.

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