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HOMOGENEOUS PERMANGANATE OXIDATION IN NON-AQUEOUS ORGANIC SOLUTION.[1)] A KINETIC STUDY ON THE DECOMPOSITION OF THE SPECTROPHOTOMETRICALLY DETECTABLE INTERMEDIATE IN THE OXIDATION OF ENDO-DICYCLOPENTADIENE

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A kinetic study on the decomposition of an organomanganese intermediate detected during the permanganate oxidation of endo-dicyclopentadiene in nonaqueous solution using quaternary ammonium salts revealed that the intermediate exists as ion pairs with quaternary ammonium ions and the stability of the intermediate inversely depends on the size of the cations.

Recently, several groups have reported spectrophotometric detection of stable intermediates in the permaganate oxidaion of alkenes in aqueous solutions[2)] and nonaqueous solutions using quaternary ammonium ions.[1,3,4)] The absorption spectra of these intermediates are quite similar to each other and similar isosbestic points were observed when the progress of the reactions was monitored. It is a recent disputed point whether these intermediates are the cyclic manganate(V) diester ([2+3] adduct of alkene and MnO_4^-), which has been postulated for a long time as the intermediate of the reaction between carbon-carbon double bonds and permanganate ion,[5)] or a soluble manganese(IV)[H_2MnO_3] species formed after rapid decomposition of the diester. The arguments for the latter are mainly based on the results of iodometric titration.[2,6)]

In connection with our previous papers[1,7)] we wish to report in this communication the results of kinetic measurement of the decomposition rates of the intermediate detected during the oxidation of endo-dicyclopentadiene (DCPD) in dichloromethane solutions using various quaternary ammonium ions.

In a typical kinetic experiment a solution of DCPD in CH_2Cl_2 (4.83×10^{-3} mol dm^{-3}) and a solution of $KMnO_4$ in CH_2Cl_2 (1.82×10^{-4} mol dm^{-3}) prepared by use of excess benzyltriethylammonium chloride (BTEAC) were first thermostated at 25.0 °C for 30 min. Aliquots (2.0 ml) of each solution were mixed together and shaken in a flask. Then the reaction mixture was rapidly transferred to a 10-mm thermostated cuvette and the reaction was followed by the measurement of the absorbance (A) at 280 nm. The data signals from the output of the spectrophotometer were input continuously (8 data/s) via a A/D converter to a microcomputer system and plots of ln A against time were recorded on a X-Y plotter (Fig. 1). After the rapid formation of the intermediate (≈50 s), the plots were observed to be linear with negative slope at the early stage of the decomposition (70-140 s) and to deviate from the straight line followed by the formation of white turbidity in the solution. The first order rate constants (k) obtained from the slopes of these linear rate plots are summarized in Table 1.

The data in Table 1 indicate that the concentration of quaternary ammonium salts has no effect on the rates of decomposition of the intermediate when the same quaternary ammonium ion is used. However, it is shown that the identity of the quaternary ammonium ion has a surprisingly large effect on the rates of reaction. For the symmetrical tetraalkylammonium ions the reaction rates were found to be proportinal to the size of the cations. Thus, as Fig. 2 indicates, there appears to be a linear relationship between the first-order rate constants and the radius of the cation.[8)]

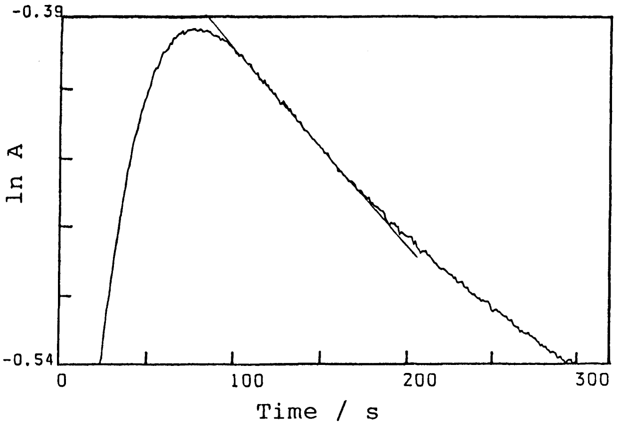


Fig. 1. Typical rate plot for the decomposition of the intermediate in CH_2Cl_2 at 25 °C.

Table 1. Rate constants for the decomposition of the detectable intermediate in the oxidation of DCPD in CH_2Cl_2 at 25 °C[a)]

Q^+X^-	$[MnO_4^-]$ / 10^{-4}mol dm^{-3}	$[Q^+X^-]$ / 10^{-4}mol dm^{-3}	[DCPD] / 10^{-3}mol dm^{-3}	k / $10^{-4}s^{-1}$
$PhCH_2N^+Et_3Cl^-$	1.82	5.02	4.83	5.35 ±0.05
	1.91	10.10	4.83	5.36 ±0.07
	1.93	20.03	4.38	5.47 ±0.32
	1.85	40.05	4.38	5.49 ±0.25
$PhCH_2N^+Et_3Br^-$	1.94	5.41	4.77	5.35 ±0.22
	1.93	19.04	4.44	5.55 ±0.26
$(Ethyl)_4N^+Br^-$	1.8-2.0	3.5-5.5	4.0-4.2	5.65 ±0.25
$(n\text{-}Propyl)_4N^+Br^-$	1.9-2.0	4.0-5.9	4.0-5.4	7.35 ±0.23
$(n\text{-}Butyl)_4N^+Br^-$	1.9-2.0	3.6-5.4	4.0-4.9	9.17 ±0.52
$(n\text{-}Pentyl)_4N^+Br^-$	1.9-2.0	4.6-5.7	4.0-5.4	9.70 ±0.81
$(n\text{-}Heptyl)_4N^+Br^-$	1.9-2.0	3.8-4.3	4.0	11.48 ±0.56

a) For the reactions using tetraalkylammonium ions measurements were repeated on solutions in the range of concentration shown with hyphen.

These observations strongly suggest that the intermediate exists as ion pairs with quaternary ammonium ions in nonaqueous solutions and the stability of the intermediate is dependent on the extent of the electrostatic interaction between the two ions. This ionic relationship is quite similar to that observed between permanganate ion and quaternary ammonium ions by Lee and Brown[3)] in dichloromethane solutions. They have shown that quaternary ammonium permanganates exist as ion pairs in nonaqueous solutions on the basis of kinetic measurements of the rate constants for the formation of the intermediate in the reactions with methyl cinnamate. The reported inverse relationship between the size of tetraalkyl ammonioum ions and the reactivity of permanganate ion can be explained in terms of the steric hindrance of the counter cations. Consequently, our result means that the ionic relationship between permanganate ion and quaternary ammonium ions is maintained during the formation of the intermediate.

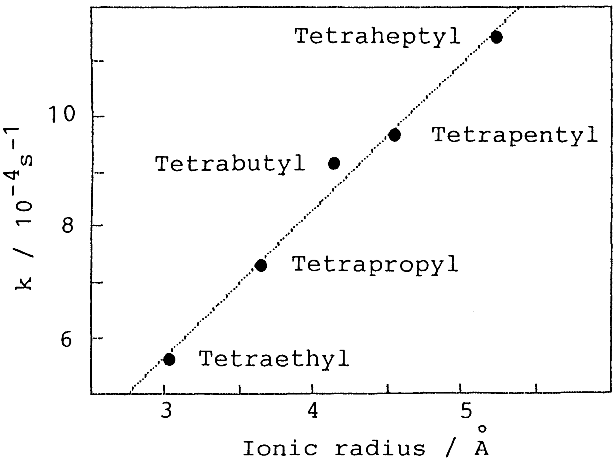
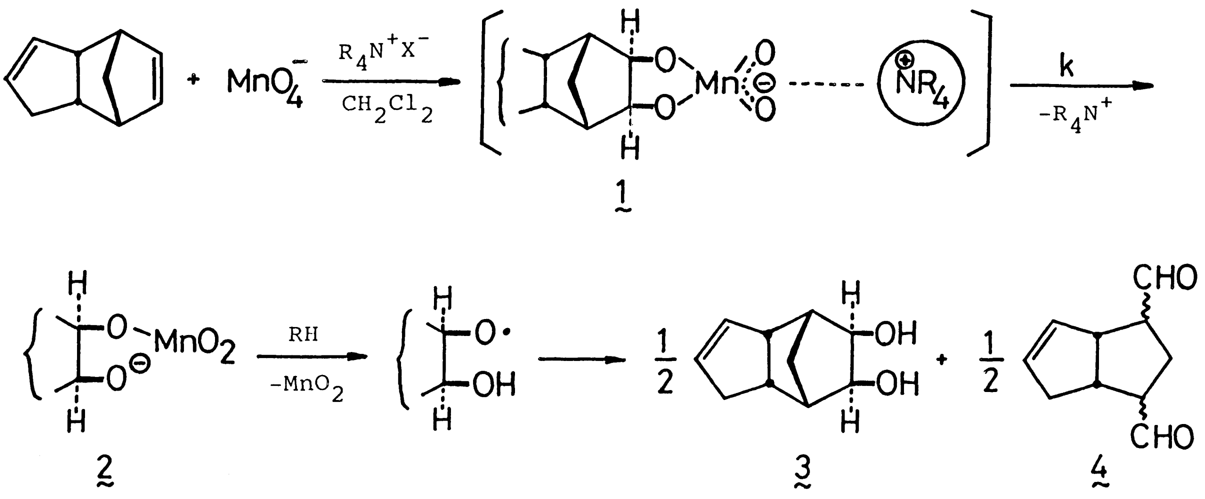


Fig. 2. Relationship between ionic size of quaternary ammonium ions and the rate constants for the decomposition of the intermediate.

It seems natural to assign the cyclic manganate(V) diester 1 to the spectrophotometrically detectable intermediate on the basis of the anionic behavior of the intermediate in nonaqueous solution. It is difficult to assume an inorganic Mn(IV) species (H_2MnO_3 or other soluble forms of MnO_2) for the intermediate in organic solution which has such a kinetic character as described above. The conclusion is consistent with the fact that treatment of the intermediate with aqueous base results in hydrolysis and yields a diol 3 as the sole product.7)

Since a 1:1 mixture of diol 3 and dialdehyde 4 was obtained together with manganese dioxide as the final products when the reaction mixture was kept anhydrous,1) one can depict a mechanism shown in Scheme 1 for a possible



Scheme 1.

decomposition pathway of the intermediate diester 1. The generation of an alkoxide ion such as 2 is in accord with the fact that the dialdehyde 4 was obtained as an isomeric mixture when the intermediate was decomposed in anhydrous condition while a single isomer was obtained when decomposed by adding aqueous solutions.[1,7]

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