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# A kinetic and mechanistic study of the thermal decomposition of nickel permanganate

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## Abstract

The isothermal anion decomposition reaction of nickel permanganate ($(Ni(MnO_4)_2 \rightarrow [NiMn_2O_5] + 1.5O_2)$) has been studied in the range 356–400 K and the phases present in the [residue] have not been fully characterized. Fractional reaction $\alpha$-time plots are sigmoid shaped, indicative of solid state nucleation and growth reactions, but the possible participation of local and temporary melt formation has not been excluded. Data obey the Avrami–Erofe'ev equation ($n = 2$) and the activation energy for salt breakdown is $100 \pm 5$ kJ mol$^{-1}$.

The first half of the reaction ($\alpha < 0.5$) proceeds relatively more rapidly ($\times 2$) under dry conditions compared with the rate in the presence of 4–5 Torr water vapour. Decomposition of nickel permanganate is more rapid than the breakdown of $MnO_4^-$ in aqueous solution, which is not influenced by the presence of dissolved nickel ions. This is an example of an autocatalytic reaction proceeding more rapidly in the solid state than the comparable homogeneous reaction in solution.

## INTRODUCTION

The thermal decomposition of potassium permanganate [1] was one of the earliest solid state reactions for which a detailed reaction mechanism was discussed. The proposed model envisaged the generation and subsequent multiplication of energetic intermediates comparable with the active radicals that participate in homogeneous chain reactions. This type of participant is today no longer regarded as an acceptable intermediate in decompositions of solids because the rapid relaxation of such energetic entities in the crystal must result in their facile deactivation. These proposals, however, stimulated interest in the characterization of the chemical

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steps participating in diverse solid state processes and the decomposition of potassium permanganate has been the subject of several subsequent studies [2]. Decomposition of $MnO_4^-$ solid solutions in inert crystalline matrices have been used to establish the role of electron transfer in permanganate breakdown [3]. The kinetic evidence for $KMnO_4$ decomposition has been reappraised in the context of microscopic observations and the role of product phase nucleation within a disintegrating crystal matrix has been discussed by several authors [4–6].

Decompositions of permanganates, other than the potassium salt, have been studied, notably those of silver and barium, but these investigations have invariably been less extensive. We considered it to be interesting to undertake a kinetic and mechanistic study of the thermal decomposition of nickel permanganate to compare behaviour of a transition metal salt with that of $KMnO_4$. An important motivation in the selection of this reactant was to determine whether such solid state reactions provide a feasible route for the preparations of mixed oxide phases, including spinels, exhibiting high catalytic activities. Aspects of the catalytic properties of these solids will be the subject of a future report. It is expected, however, that such catalysts prepared at low temperatures may possess high surface areas, incorporate high vacancy concentrations and retain oxygen in stoichiometric excess, all features found in active oxidation phases.

Nickel permanganate, $Ni(MnO_4)_2 \cdot 6H_2O$, was selected for our first study because it is easily prepared [7] and decomposition could be expected to yield $NiMn_2O_4$. The present report is concerned with anion breakdown in this reactant and comparison of the observed behaviour with that of other permanganates. Because the present reaction proceeded at lower temperatures than for the alkali salts our measurements have enabled comparative kinetic observations to be made for the decomposition of $MnO_4^-$ in aqueous solution in addition to our principal interest in the decomposition of solid $Ni(MnO_4)_2$ in vacuum and in low pressures of water vapour. Mechanistic investigations included some microscopic examinations of reactant textures.

## EXPERIMENTAL

### *Rate measurements*

All kinetic studies were completed under isothermal conditions. A known mass of reactant, retained in a small glass tube, was evacuated (less than $10^{-4}$ Torr for 20 min) before being introduced into the constant temperature reaction zone of the glass apparatus after isolation from the pumps. The progress of decomposition was monitored from the pressure of gas evolved measured using a Baratron MKS 222B gauge. Two complementary sets of experiments were made using a 78 K cold trap (product $O_2$

only) and no trap (both oxygen and water vapour). Output from the diaphragm gauge was supplied to a computer programmed to record pressure at appropriate time intervals (subject to the condition that a prespecified amount of reaction had occurred) and the reaction zone temperature. The apparatus used was identical with that previously described [8].

Extent of reaction was expressed as fractional reaction $\alpha = p/p_f$, where $p$ is the pressure measured in the apparatus at time $t$ and $p_f$ represents the completion of reaction. The computer programme included a facility for testing obedience of data to kinetic expressions characteristic [2] of solid decompositions $f(\alpha) = kt$.

### Reactant solids

Nickel permanganate was prepared by slowly mixing together nearly saturated solutions of barium permanganate and nickel sulphate containing the required 2:1 molar ratio of the required ions

$$Ba(MnO_4)_2 + NiSO_4 \rightarrow Ni(MnO_4)_2 + BaSO_4$$

The precipitated barium sulphate was immediately removed by filtration and the solution slowly evaporated at low (about 290 K) temperature. The crystals which subsequently appeared were separated by filtration, superficial water was removed by filter paper and the hydrated salt was dried in air. Samples were always stored under cool conditions in the dark and studied soon after preparation to minimize deterioration during storage. Three samples of salt (Preparations 1, 2 and 3) were investigated during the kinetic measurements; these differed only in the extent of solution evaporation before harvesting.

Reactant analyses were complicated by the deviation from stoichiometry; water was very readily lost from salt Preparations, for which the composition ($Ni(MnO_4)_2 \cdot 4.5H_2O$) was appreciably different from that of the expected [7] hexahydrate. The constituent manganese agreed with the stoichiometric requirement and repeated electron microprobe analyses of the residue showed the Ni:Mn elemental ratio to be $1.0:1.9 \pm 0.15$.

## RESULTS

### Reaction stoichiometry

Mean yields of gaseous products were measured as $4.53H_2O$, rapidly released (less than 5 min) on heating the salt above 360 K in vacuum, and

$1.54O_2$ representing completion of the subsequent salt decomposition. The stoichiometry of the two steps in reaction may, therefore, be expressed as

$$Ni(MnO_4)_2 \cdot 4.5H_2O \rightarrow Ni(MnO_4)_2 + 4.5H_2O$$

$$Ni(MnO_4)_2 \rightarrow [NiMn_2O_5] + 1.54O_2$$

The present study is concerned with the second (anion breakdown) reaction. The mean stoichiometric values reported here were obtained from 32 experiments in which the final pressures were determined at the end of kinetic studies of the reactions of known reactant masses in the calibrated volume of the vacuum apparatus. Mass losses expected from evolution of these amounts of water and oxygen (21.5% + 13.0% = 34.5%) are in acceptable agreement with the mean overall measured mass loss (32.3%) and values obtained thermogravimetrically (23% + 11% = 34%).

The above equation, therefore, acceptably represents the reaction stoichiometry though the identity of the phases present in the residue have not yet been satisfactorily characterized; possibilities include (inter alia) NiO + $2MnO_2$ and $NiMnO_3 + MnO_2$.

## *Kinetic measurements*

### *Decomposition in vacuum*

Representative fractional reaction ($\alpha$)–time plots for the isothermal decomposition of nickel permanganate for the reaction yielding product oxygen only (78 K trap present) at four temperatures are shown in Fig. 1.

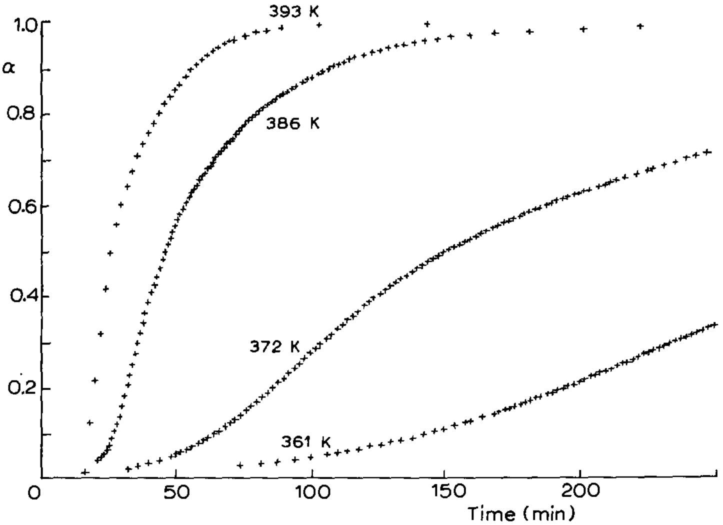


Fig. 1. Representative fractional reaction ($\alpha$)–time plots for the isothermal decomposition of nickel permanganate at four different temperatures. These measurements are for the evolution of product oxygen only from samples of Preparation 1 using a 78 K cold trap.

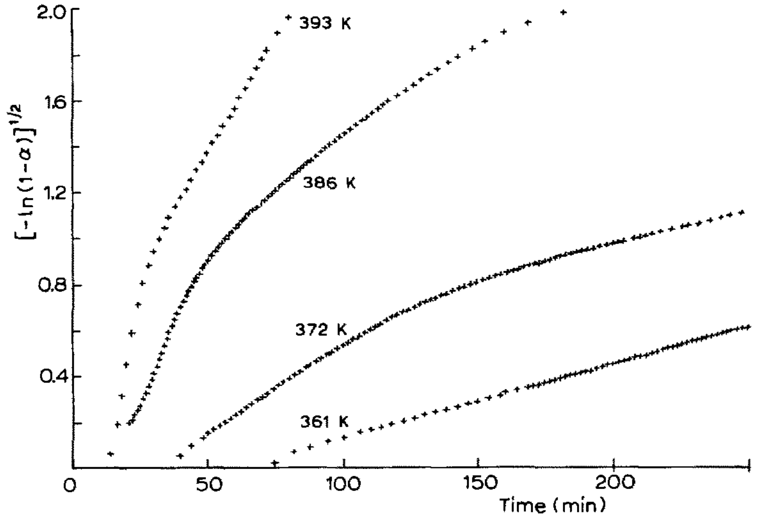


Fig. 2. Plots of $[-\ln(1-\alpha)]^{1/2}$ against time for the data in Fig. 1. Linearity of these plots shows obedience to the Avrami–Erofe'ev equation with $n = 2$.

An initial deceleratory process, completed at $\alpha = 0.035 \pm 0.010$, preceded the main reaction. The main anion decomposition reaction exhibited sigmoid shaped $\alpha$–time curves (Fig. 1). A short initial induction period was followed by the acceleratory process. There was a reduction in rate at around the half-way stage followed by a pronounced deceleratory process. This reaction obeyed the Avrami–Erofe'ev equation with $n = 2$ [2]

$$[-\ln(1-\alpha)]^{1/2} = kt$$

(after subtraction of the contribution from the initial process) and typical obedience plots are shown in Fig. 2. Rate constants for the first half of reaction (linear plots between $0.03 < \alpha < 0.45/0.53$) were significantly greater (about 2 × ) than those for the second half of reaction ($0.50/0.55 < \alpha < 0.95$). Behaviour in the intermediate region was somewhat variable, as is evident from Fig. 2, the curved portion being short in some reactions but representing up to about 8% of the reaction in others.

The above results were obtained for Preparation 1, and data measured for the reactions of both Preparations 2 and 3 were identical within experimental error. Rate coefficients from all three salts, acceleratory and deceleratory periods, were close to two parallel lines on the Arrhenius plot (Fig. 3). The activation energies were calculated as $100 \pm 5$ kJ mol$^{-1}$, 356–400 K and frequency factors were $10^{14.0}$ s$^{-1}$ and $10^{13.7}$ s$^{-1}$ for the acceleratory and deceleratory phases of decomposition respectively.

*Decomposition in water vapour*

During experiments in which no cold trap was maintained on the apparatus, between heated salt and gauge, decomposition proceeded in an

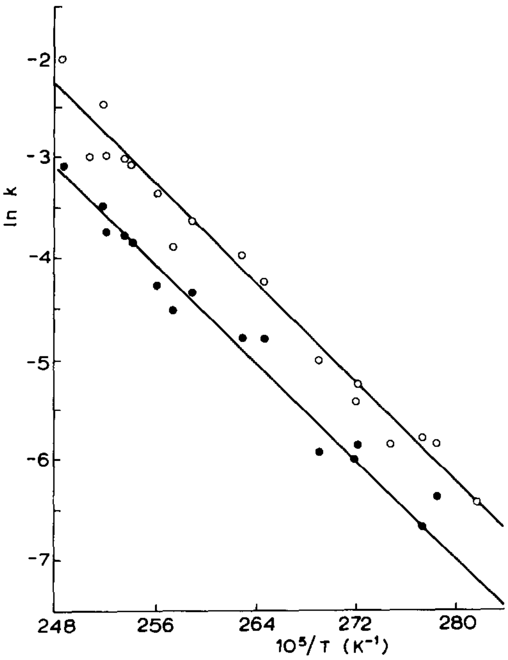


Fig. 3. Arrhenius plots for the decomposition of nickel permanganate in the presence of a 78 K cold trap using Avrami–Erofe'ev equation ($n = 2$) [2] rate constants. The upper and lower lines refer to the acceleratory and deceleratory period of reaction.

atmosphere containing a small water vapour pressure, typically 4–5 Torr $H_2O$. In all kinetic analyses of these decompositions, the pressure rise identified as the rapid initial dehydration ($< 5$ min) was subtracted. The $\alpha$–time curves for the subsequent anion breakdown rate process were sigmoid shaped and differed from the previous series in that the acceleratory phase was relatively less pronounced. Typical plots for the reactions of four samples of Preparation 1 at different temperatures are shown in Fig. 4. Data again obeyed the Avrami–Erofe'ev equation but obedience was equally satisfactory for both $n = 2$ and $n = 3$, with a single straight line between $0.03 < \alpha < 0.95$. The fit for the latter is shown in Fig. 5.

Magnitudes of rate constants (Avrami–Erofe'ev, $n = 2$) for decompositions of all three nickel permanganate preparations, 356–400 K, in water vapour were identical, within experimental error, with those for the second rate process under dry conditions. This identity is illustrated in Figs. 6 and 7. Figure 6 shows the Avrami–Erofe'ev plot, $n = 2$, for decomposition of Preparation 1 at 386 K under conditions which differed only in the inclusion of a 78 K trap for the rate process showing the initial relatively rapid acceleratory stage. It is evident that the extended linear plot for the reaction in water vapour is parallel with the second stage of the dry reaction. Figure 7 is an Arrhenius plot (Avrami–Erofe'ev equation, all

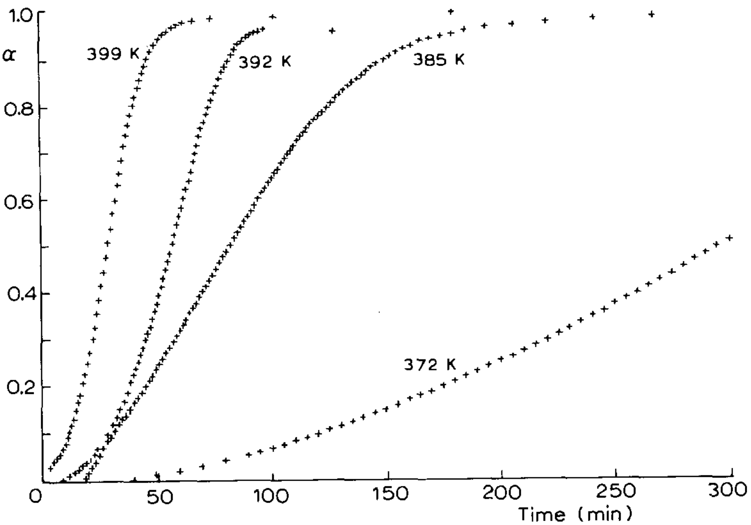


Fig. 4. Representative $\alpha$–time plots for the isothermal anion decomposition reaction of nickel permanganate in 4–5 Torr water vapour at four temperatures. The pressure rise from the rapid initial dehydration step has been subtracted before calculation of $\alpha$.

$n = 2$ rate constants) for the decompositions of all three salt Preparations without a cold trap (●, obedience over the greater part of reaction, $0.03 < \alpha < 0.95$) together with those for reactions using a 78 K trap (○, obedience during the second part of reaction, about $0.5 < \alpha < 0.95$). No distinction between these two families of points is evident, the rate of anion breakdown throughout reactions in water vapour is the same as that for the

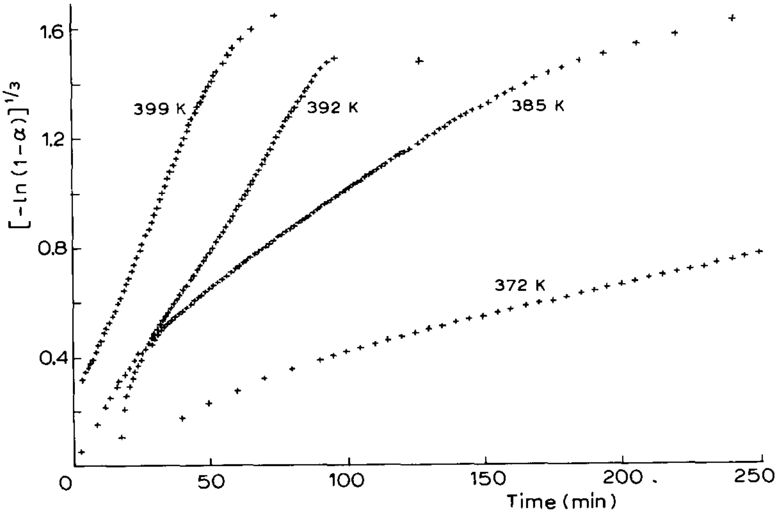


Fig. 5. Avrami–Erofe'ev ($n = 3$) equation plots for the data in Fig. 4.

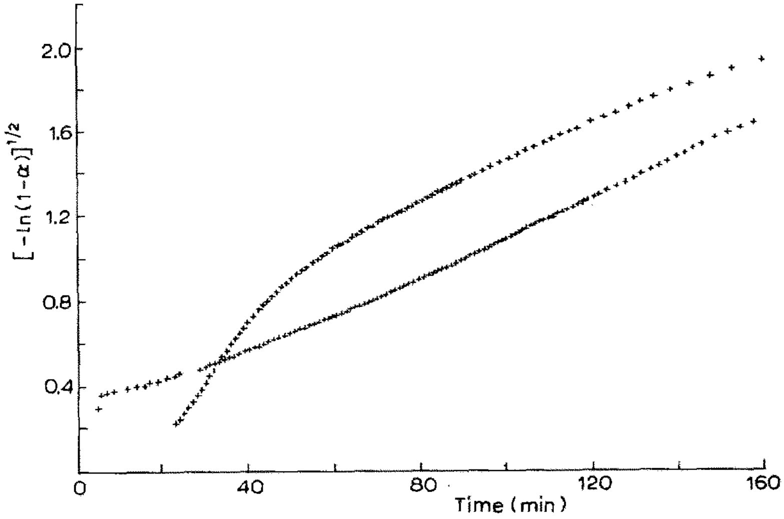


Fig. 6. Avrami–Erofe'ev ($n = 2$) equation plots for the decomposition of nickel permanganate at 386 ± 1 K in the presence of 4–5 Torr water vapour (the almost linear plot) and under dry conditions (plot with two linear regions). The close agreement of the rate constants during the latter part of reaction and the difference in initial behaviour are discussed in the text.

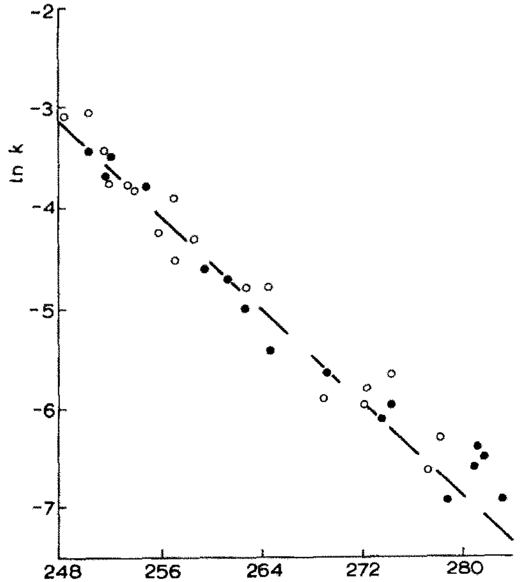


Fig. 7. Arrhenius plot for Avrami–Erofe'ev ($n = 2$) equation rate constants for the decomposition of nickel permanganate under dry conditions, (○, obedience during second part of reaction only, about $0.5 < \alpha < 0.95$, lower line in Fig. 3) and in 4–5 Torr water vapour (●, obedience over most of the reaction, $0.03 < \alpha < 0.95$). The line is that in Fig. 3.

second part of the dry reaction. Again the activation energy is close to 100 kJ $mol^{-1}$ and no difference in behaviour was detected between the three salt Preparations.

### $MnO_4^-$ *decomposition in solution*

Comparative studies were undertaken of the decomposition of the permanganate ion (0.01 M) in a boiling aqueous solution (373 K) also containing $Ni^{2+}$ (0.05 M). This homogeneous reaction, involving hydrated ions, proceeded much less rapidly (×0.05) than the solid state decomposition described above. Moreover, the homogeneous reaction rate was similar to that of $MnO_4^-$ breakdown in potassium permanganate solution alone (in the absence of $Ni^{2+}$). This suggests that in the aqueous medium the nickel ion does not promote permanganate breakdown, which occurs more rapidly in the absence of water solvent.

## DISCUSSION

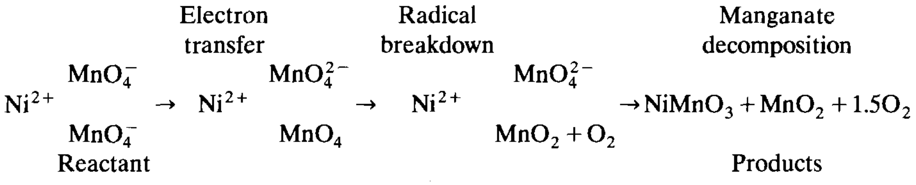
Electron microscopic examination of the dehydrated reactant and the decomposition residue gave evidence of the occurrence of some crystallite sintering but the demonstration of the participation of fusion was not conclusive [8]. However, identical kinetic characteristics for reactions of all three salt Preparations and the absence of any change in rate on reactant crushing indicates that particle size does not exert a dominant influence on reaction rate. The sigmoid shaped $\alpha$–time curve is characteristic of solid state nucleation and growth processes, but may apply to reactions where there is local and/or partial melt formation [8,9].

Comparison of the temperature interval of the present study of nickel permanganate decomposition (356–400 K) with other permanganates [2] shows that it is appreciably less stable than the salts of the alkali and alkaline earth metals and somewhat less stable than the silver salt. There appears to be agreement in the literature that electron transfer within the anion sublattice is an essential step in the decompositions of solid permanganates [2,3,10]

$$2MnO_4^- \rightleftharpoons MnO_4^{2-} + MnO_4$$

$$MnO_4 \rightarrow MnO_2 + O_2$$

Taking this as the central theme of our mechanistic discussion, we also note that, unlike the alkali metals, the nickel cation is capable of oxidation. This is not, however, regarded as contributing to reaction because formation of the unstable breakdown intermediate must be opposed by such an electron donation step in the crystal ($Ni^{2+} \xrightarrow{-e} Ni^{3+}$, positive hole generation). Electron transfer steps yield the potentially stable anions ($MnO_4^- \xrightarrow{+e} MnO_4^{2-} \xrightarrow{+e} MnO_4^{3-}$), which do not, of course, yield oxygen, the product monitored here in kinetic measurements. Accordingly we propose the following reaction mechanism to explain the present observations.



$$\begin{array}{ccccccc} & \text{Electron} & & \text{Radical} & & \text{Manganate} \\ & \text{transfer} & & \text{breakdown} & & \text{decomposition} \\ \begin{matrix} & MnO_4^- \\ Ni^{2+} & \\ & MnO_4^- \end{matrix} & \rightarrow & \begin{matrix} & MnO_4^{2-} \\ Ni^{2+} & \\ & MnO_4 \end{matrix} & \rightarrow & \begin{matrix} & MnO_4^{2-} \\ Ni^{2+} & \\ & MnO_2 + O_2 \end{matrix} & \rightarrow NiMnO_3 + MnO_2 + 1.5O_2 \\ \text{Reactant} & & & & & \text{Products} \end{array}$$

The activation energy is identified with the electron transfer step $2MnO_4^- \rightleftharpoons MnO_4^{2-} + MnO_4$. This value is close to that for the decompositions of other permanganates [11]. The manganate intermediate ($NiMnO_4$), if formed during the decomposition of $KMnO_4$, similarly undergoes subsequent breakdown; characterizations of the residual products from $KMnO_4$ decomposition have, up to the present, been incomplete [10].

Under dry conditions the first part of the single overall rate process is relatively rapid compared to the reaction in small water vapour pressures (Fig. 6). Both processes may, however, be identified with a common rate controlling step because the activation energy values are the same. We have no direct experimental evidence to explain the differences in rate, though the following are acceptable mechanisms.

If reaction proceeds exclusively in the solid state, adsorbed water molecules may influence the reactivity of potential nucleation sites, active growth nuclei being generated at larger numbers of sites under dry conditions. Such behaviour readily explains the doubling of reaction rate. Alternatively, if the reaction involves participation of local and temporary melt formation, the involvement of surface water may similarly influence the concentration of electronic imperfections in the surface zone. This effect is greatest at low $\alpha$ because later chemical change advancing within the reactant-product assemblages will be less influenced by surface effects at the outer layer of the envelope.

The overall rate of salt decomposition is identified, therefore, as being controlled by the concentration of electronic imperfections. This is consistent with the observation that reaction in the crystal proceeds more rapidly than that in an aqueous solution where the presence of nickel ions (hydrated) does not accelerate the rate of $MnO_4^-$ breakdown. This is an interesting result, identifying a heterogeneous, solid state, reaction that is more rapid than the comparable homogeneous process. The forces of crystal coherence apparently do not stabilize the anion in this particular reaction, in contrast with the pattern of behaviour believed to apply to many other reactions involving initially crystalline reactions.

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