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# KINETICS OF THE THERMAL DECOMPOSITION OF AQUEOUS MANGANESE(II) NITRATE SOLUTION

P. K. GALLAGHER AND D. W. JOHNSON
*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974 (U. S. A.)*

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## ABSTRACT

Isothermal weight studies were performed upon aqueous solutions of manganese(II) nitrate. The loss of water followed a first order rate law with activation energies varying from 6 to 10 kcal/mole depending upon the atmosphere. The resulting anhydrous nitrate decomposed to form manganese(II) oxynitrate in accordance with the Erofeev equation with $n = 4$. The activation energies are 20–25 kcal/mole and show little variation with atmosphere. The resulting oxynitrate decomposed to form manganese(IV) oxide. The rate fits several expressions satisfactorily but a contracting area form is chosen as generally best. The activation energy is about 12 kcal/mole lower in the presence of moisture but this effect upon the rate is partially offset by a substantial decrease in the preexponential term. The manganese(IV) oxide loses oxygen to form manganese(III) oxide. The best rate law is the Jander equation and activation energies are in the range of 47–57 kcal/mole.

## INTRODUCTION

A semiconducting layer of manganese(IV) oxide is frequently used as a counter-electrode in the preparation of metal oxide capacitors. One technique for forming such a layer is to dip the porous anodized metal electrode into an aqueous solution of manganese(II) nitrate and then thermally decomposing the adhering solution to manganese(IV) oxide. Consequently, the nature and kinetics of such a decomposition are of considerable interest.

The general nature and stoichiometry of such a decomposition has been established in earlier work[1]. The solution loses water to form a glassy appearing solid having a composition of $Mn(NO_3)_2 \cdot 2H_2O$. This material then decomposes beginning around 150°C to form a very transient intermediate, $MnONO_3$. This manganese(III) oxynitrate then decomposes at slightly higher temperatures to form the desired manganese(IV) oxide. It was observed that the presence of moisture in the atmosphere will lower the decomposition temperature of the manganese(III) oxynitrate.

It is the purpose of this paper to investigate the rate at which these various steps take place. To accomplish this, isothermal kinetic studies were performed in both moist and dry atmospheres and at a variety of temperatures to allow for the calculation of activation energies.

## EXPERIMENTAL PROCEDURE AND RESULTS

### *Materials*

Aqueous manganese(II) nitrate was obtained from the Fisher Chemical Company, reagent grade lot no. 713972 (density = 1.55) and the Lehigh Valley Chemical Company, capacitor grade (density = 1.65). Small portions of these solutions were evaporated and then heated at 250 °C in air overnight. Table I presents the results of emission spectrographic analysis of the residues. There was no difference in behavior of the two solutions other than water content and consequently only data for the Fisher material is reported upon further.

TABLE I

EMISSION SPECTROGRAPHIC ANALYSIS OF RESIDUES FROM COMMERCIALLY AVAILABLE AQUEOUS SOLUTIONS OF $MnO_2$

| *Wt. %* | *Fisher Chemical Company* | *Lehigh Valley Chemical Company* |
|---|---|---|
| $10^{-1}x$ | Mg | Mg |
| $10^{-3}x$ | Cu | |
| $10^{-4}x$ | Ca, Fe, K[a] | Ca, Cu, Fe[a] |

[a] Low part of range.

### *Isothermal weight change*

A Perkin–Elmer thermobalance was modified to give weight and temperature as a function of time[2,3]. For these isothermal studies, only the weight portion was operated. The weight was averaged over predetermined constant intervals of time and automatically punched on paper tape. Time intervals ranged from 3 to 30 sec depending upon the rate of weight loss. The temperature of each experiment was determined by measuring the control voltage of the Perkin–Elmer UU-1 controller and comparing it with the calibration equation. This equation was based upon the use of magnetic standards as previously described[3]. The heating rate for the calibration experiment was 1.25 °C/min.

Approximately 0.01 ml of solution was placed in a shallow cylindrical platinum pan (4 mm diameter, 1 mm deep). Both wet and dry oxygen or nitrogen was passed over the sample at about 25 ml/min. The input gas was passed through a column of silica gel and, if a wet atmosphere was desired, through a bubbler which saturated the gas with water vapor at room temperature.

An initial sample weight was obtained as quickly as possible and then the temperature was raised at a rate of approximately 320 °C/min to a temperature in the range of 100–135 °C. The data acquisition unit was started as soon as the UU-1 controller reached the control point. Data were collected at this temperature until essentially constant weight was reached at which time data taking was stopped and the temperature raised in the same manner to 150–200 °C. Data were again collected until constant weight. The sample was raised to 300°C and the weight recorded after it had become constant. The temperature was then raised to between 450 and 500°C and rate data accumulated to constant weight. The sample was finally heated to 1000°C and the final weight recorded. In this manner there were three sets of weight *versus* time data determined for each sample. These corresponded to the initial dehydration step (120–155°C), the decomposition to manganese(IV) oxide (160–210°C), and the reduction of this material to manganese(III) oxide (450–500°C).

*Computer analysis*

The weight data on the tape were transferred to cards using a GE-635 computer. These data cards served as the input for three stages of computer processing. The first stage was to obtain a graphical output of the weight as a function time. Fig. 1 is an example of such an output for a sample run in dry nitrogen. The upper portion shows the isothermal weight loss at 152°C associated with dehydration. The middle portion at 196°C corresponds to the loss of water of crystallization and the two step

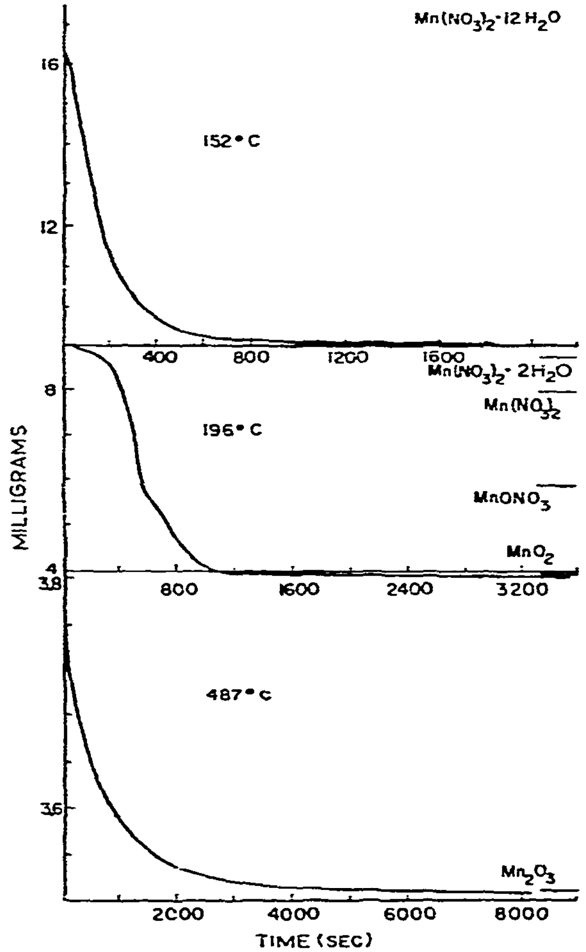

Fig. 1. Weight *versus* time curves.

decomposition of the anhydrous nitrate. The bottom portion gives the weight loss data associated with the reduction of manganese(IV) oxide to manganese(III) oxide at 487 °C. Plots of this type gave an overall view or check on the experiment and served too as the basis for the determination of the initial and final weights for each step.

The second stage of data handling consisted of utilizing the initial and final weights for each step to determine values of $\alpha$, the fraction reacted. The computer having calculated the values of $\alpha$ for each point then plotted these to conform to the eighteen equations given in Table II. These equations were selected because of their

TABLE II

KINETIC EQUATIONS USED IN THE COMPUTER ANALYSIS

| | |
|---|---|
| Power law | $\alpha^n$; $n = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}$, 1 and 2 |
| Contracting geometry | $1-(1-\alpha)^{1/n}$; $n = 2$ and 3 |
| Erofeev | $[-\ln(1-\alpha)]^{1/n}$; $n = 1, \frac{3}{2}, 2, 3$ and 4 |
| 2D Diffusion controlled | $(1-\alpha)\ln(1-\alpha)+\alpha$ |
| 3D Diffusion controlled | $(1-\frac{2}{3}\alpha)-(1-\alpha)^{\frac{2}{3}}$ |
| Jander | $[1-(1-\alpha)^{\frac{1}{3}}]^2$ |
| Prout–Tompkins | $\ln\left(\frac{\alpha}{1-\alpha}\right)$ |
| Second order | $\frac{1}{1-\alpha}-1$ |
| Exponential | $\ln\alpha$ |

frequent application to the decomposition of solids. Appropriate equations were determined by visual inspection of the computer output plots for their linearity. As examples, the family of lines resulting from each of the overall reaction are shown in Figs. 2–5 for the data taken in wet nitrogen. It was frequently disconcerting to find that no single equation was obviously best at this point. Fig. 6 is an example where the visual degree of fit is quite comparable. These curves are over the range of $\alpha$ from 0.2 to 0.9 for the decomposition of the oxynitrate at 177 °C in dry nitrogen. It is necessary to back off to an $\alpha$ value of 0.2 because of the overlap of this reaction with its predecessor. The choice of equation was then based on the exact degree of

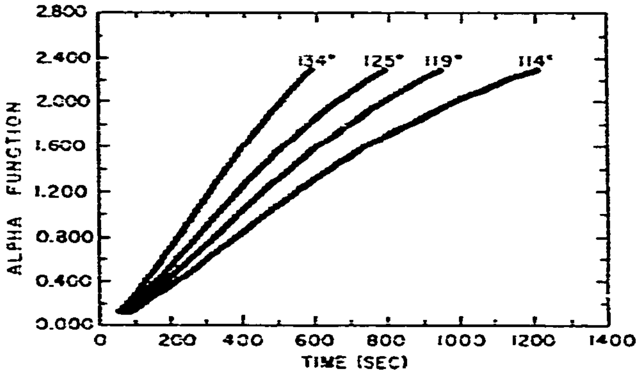

Fig. 2. Plots of $-\ln(1-\alpha)$ *versus* time for the dehydration of aqueous manganese(II) nitrate.

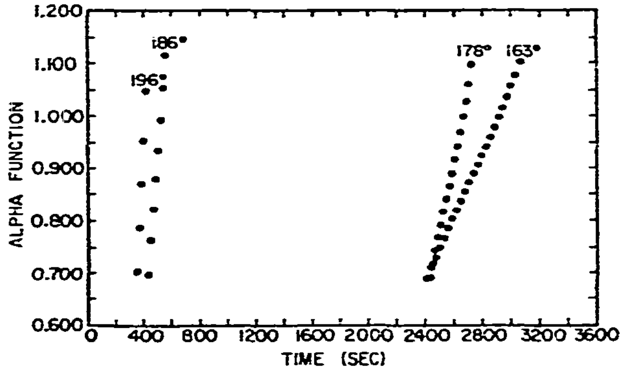

Fig. 3. Plots of $[-\ln(1-\alpha)]^{\frac{1}{2}}$ *versus* time for the reaction $Mn(NO_3)_2 \rightarrow MnONO_3 + NO_2$.

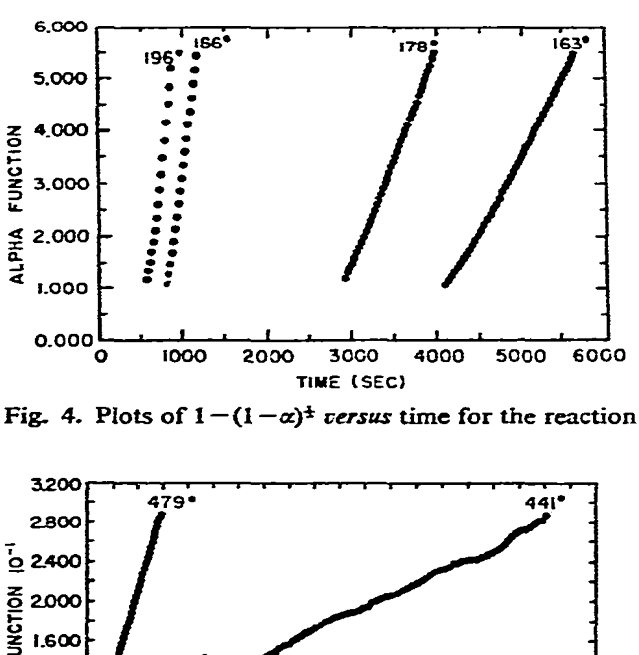

Fig. 4. Plots of $1-(1-\alpha)^{\frac{1}{3}}$ *versus* time for the reaction $MnONO_3 \rightarrow MnO_2 + NO_2$.

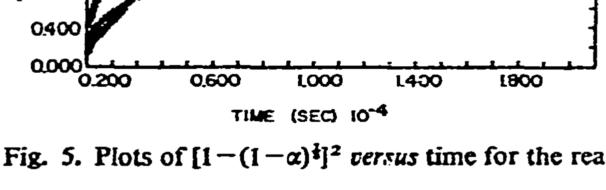

Fig. 5. Plots of $[1-(1-\alpha)^{\frac{1}{3}}]^2$ *versus* time for the reaction $2MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$.

fit determined by the standard deviation arising from the computer calculation of $k$ in the third stage of processing.

After the most likely kinetic equation or equations had been selected for each reaction the appropriate experimental data are reprocessed using a third program to fit the best straight lines using a least squares technique. The printed output gives the best value of $k$ and a standard deviation in terms of both $F(\alpha)$ and $\alpha$. The standard deviation in $\alpha$ is used to determine which equation is most suitable for those cases where several equations were considered.

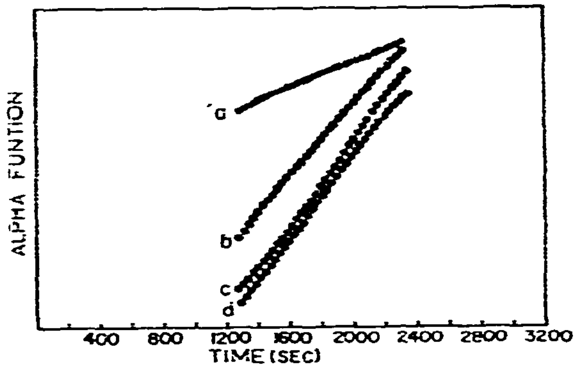

Fig. 6. Plots of several $F(\alpha)$'s *versus* time for the reaction $MnONO_3 \rightarrow MnO_2$, at 177°C, in dry $N_2$; (a) $F(\alpha) = \ln(\alpha/1-\alpha)$; (b) $F(\alpha) = -\ln(1-\alpha)^{\frac{1}{2}}$; (c) $F(\alpha) = 1-(1-\alpha)^{\frac{1}{3}}$; (d) $F(\alpha) = 1-(1-\alpha)^{\frac{1}{2}}$.

A final program was devised to plot the values of log $k$ *versus* the reciprocal of the absolute temperatures (Arrhenius plot) and a least squares fit was made to determine the best straight line. The resulting activation energies and preexponential terms were printed out along with the plot. These values are listed in Table III. Fig. 7 shows the family of Arrhenius plots for the decomposition series in wet nitrogen.

As previously mentioned the data can frequently be fit moderately well by several equations. In all cases the activation energies show very little variation with

TABLE III

VALUES OF ACTIVATION ENERGY AND PREEXPONENTIAL FROM THE ARRHENIUS EQUATION $k = Ae^{-\Delta H^*/RT}$

| *Equations* | *Atmosphere* | *ΔH** *(Kcal/mole)* | *A (sec⁻¹)* |
|---|---|---|---|
| $Mn(NO_3)_2 \cdot xH_2O \rightarrow Mn(NO_3)_2 \cdot yH_2O + (x-y)H_2O$ | Dry $N_2$ | 6.4 | $1.2 \times 10$ |
| $kt = -\ln(1-\alpha)$ | Wet $N_2$ | 9.7 | $7.5 \times 10^2$ |
| | Dry $O_2$ | 8.9 | $2.8 \times 10^2$ |
| | Wet $O_2$ | 7.7 | $5.6 \times 10$ |
| $Mn(NO_3)_2 \rightarrow MnONO_3 + NO_2$ | Dry $N_2$ | 21.7 | $6.2 \times 10^9$ |
| $kt = [-\ln(1-\alpha)]^{\frac{1}{2}}$ | Wet $N_2$ | 25.0 | $1.9 \times 10^9$ |
| | Dry $O_2$ | 21.0 | $2.0 \times 10^7$ |
| | Wet $O_2$ | 20.2 | $8.5 \times 10^6$ |
| $MnONO_3 \rightarrow MnO_2 + NO_2$ | Dry $N_2$ | 32.8 | $3.1 \times 10^{12}$ |
| $kt = 1-(1-\alpha)^{\frac{1}{3}}$ | Wet $N_2$ | 20.6 | $5.4 \times 10^6$ |
| | Dry $O_2$ | 29.0 | $1.3 \times 10^{11}$ |
| | Wet $O_2$ | 17.8 | $2.9 \times 10^5$ |
| $2MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$ | Dry $N_2$ | 53.1 | $6.2 \times 10^{11}$ |
| $kt = [1-(1-\alpha)^{\frac{1}{3}}]^2$ | Wet $N_2$ | 47.5 | $1 \times 10^{10}$ |
| | Dry $O_2$ | 56.5 | $1.2 \times 10^{11}$ |
| | Wet $O_2$ | 50.7 | $8.0 \times 10^9$ |

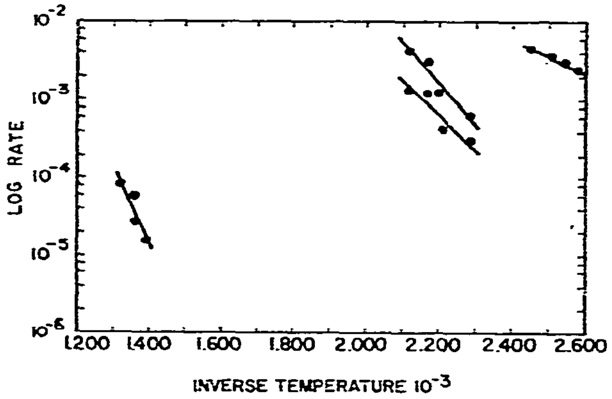

Fig. 7. Arrhenius plots for all four reactions in wet nitrogen.

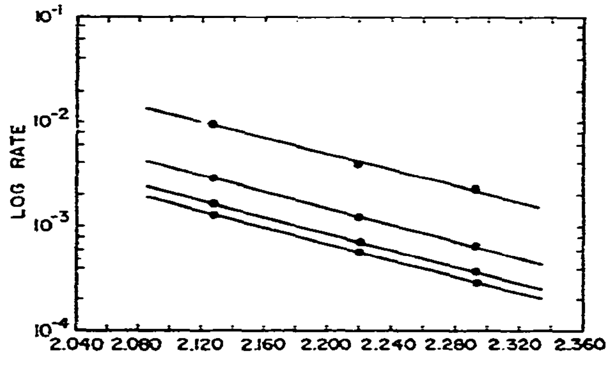

Fig. 8. Arrhenius plots for the reaction $MnONO_3 \rightarrow MnO_2 + NO_2$ in wet $O_2$. Values of $\Delta H = 17.8 + 0.05$ kcal/mole, $A = 2.90 \times 10^5$ to $1.81 \times 10^6$.

choice of rate equation. As an example the Arrhenius plots using rate constants from four different equations are shown in Fig. 8 for the decomposition of the oxynitrate in wet oxygen. The differences are reflected in the preexponential term and the activation energy is virtually independent of the equation.

## DISCUSSION

The breaks in the isothermal weight curves support the general nature of the reaction previously proposed[1]. This is particularly obvious for the manganese(III) oxynitrate as shown in Fig. 1. The overlap of the three reactions in the middle zone complicates the treatment of the data and introduces considerable uncertainty to the exact values. The separation of a progression of reactions, by redefining initial and final weights into a series of individual decompositions has been done in similar studies[4,5]. It, nevertheless, is a highly idealized treatment which assumes that all of the intermediate is formed before any of it begins to react. For this reason, the beginning of the first reaction and the end of the second were stressed in making a determination of the rate law and constant.

Besides the problem of overlapping reactions, there are several other difficulties associated with the interpretation of the kinetics. One of the major ones concerns the nonideal or uncontrolled nature of the sample. There are no nicely sized fractions or pelletized samples to simplify the geometrical considerations. This is an attempt to deal with a real situation and consequently the starting particle size and morphology is restricted to that produced by the preceding evaporation or decomposition. Since several kinetic experiments are performed on the same sample, it means that there will be some variations in the thermal history among the samples. The fact that the data are frequently fit reasonably well by several kinetic equations also urges caution in the interpretation of the kinetics in terms of a specific geometric mechanism. Fig. 8, however, is reassuring with respect to values of the activation energy.

The individual reaction steps will now be discussed with those basic considerations in mind. The dehydration step is the single reaction which exhibits a unique rate law. The data very decidedly indicate a first order decomposition such that

$$kt = -\ln(1-\alpha)$$

This means that the reaction is proportional to the amount of water remaining or more correctly the relative population of water molecules in the exposed surface layer. The observed activation energies, 6–10 kcal/mole, may be determined by at least two basic processes depending upon which is the rate determining step. One is the actual chemical process of transferring a water molecule at the surface of the solution into the vapor phase. The heat of vaporization for pure water in this temperature range is about[6] 9 kcal/mole. Since the process is endothermic this must represent a minimum activation energy for the process. The vapor pressure of water over a concentrated solution such as employed in this work is lower than over pure water and would imply an even higher energy of activation.

Another possible mechanism would involve the very rapid evolution of water from the surface and the diffusion of bulk water to the surface as the rate determining step. Here again the rate would be expected to follow a first order rate law since the concentration gradient would be the driving force for diffusion. With the observed range of activation energies it is not possible to determine which mechanism is operative or predominant.

The preexponential terms, as given in Table III, are very markedly lower than for the other processes. Assuming that the reactions take place at the exposed surface the large difference can be at least partially explained. The exposed surface area of the solution is of the order of $10^{-3}$ $m^2/g$. This compares to the surface areas of about 3 $m^2/g$ at the end of the decomposition of the manganese(II) nitrate[1]. This factor is nearly enough to explain the difference between the preexponential terms for the dehydration and the decomposition of manganese(III) oxynitrate in wet nitrogen or oxygen.

The stage between the glassy hydrate of manganese(II) nitrate and the anhydrous material is not treated because of the uncertainty of the starting stoichiometry. The decomposition of the anhydrous nitrate to form manganese(III) oxynitrate obeys the

Erofeev equation with $n=4$, $kt=[-\ln(1-\alpha)]^{\frac{1}{4}}$, best over all but also conforms reasonably well to the power law with an optimum value of $n$ between 1 and 2. Activation energies are virtually independent of the rate equation used. There does not appear to be a great dependence of the observed activation energy upon atmosphere. The actual values of the rate constant, however, are significantly smaller in oxygen because of the smaller preexponential term. No evidence is available to establish whether this lower preexponential term is due to a reduced surface area or reaction probability in oxygen.

In contrast the decomposition of manganese(III) oxynitrate shows a very marked and complex dependence upon atmosphere. The activation energy and preexponential are slightly lower in oxygen as in the previous reaction but, more importantly, there is a very pronounced effect of moisture upon both of these values. The effects are opposed so that there is actually a crossover in the relative rates dependent upon temperature. The preexponential term is much smaller presumably due to a reduction in surface area arising from improved crystallinity and increased sintering in the presence of moisture. This reduces the reaction rate in the presence of moisture, however, this improved crystallinity means that there is less energy stored in the product phase and consequently the activation energy is lower and approaches the actual thermodynamic enthalpy of the reaction[7]. This reduced energy of activation results in a more rapid increase in the rate constant with increasing temperature. In a nitrogen atmosphere this effect predominates above ~190°C and the rates are more rapid in the presence of moisture. Below ~190°C the reduced surface area predominates and the reaction is slower in the presence of moisture.

The reduction of the manganese(IV) oxide also exhibits smaller preexponential terms in moist atmospheres than in dry. This may again be a surface area effect. The activation energies are generally lower than those reported by Hegedus *et al.*[8]. They report values from 86 to 101 kcal/mole depending upon the activity of the manganese(IV) oxide. The value, 47–57 kcal/mole, reported in Table III, however, is still well above that for the reaction

$$2MnO_2 \rightarrow Mn_2O_3 + \tfrac{1}{2}O_2 \qquad \Delta H_{800\,^{\circ}K} = +19.2 \text{ kcal/mole} \qquad \text{(Ref. 9)}$$

It would appear that the manganese(III) oxide formed must be in a highly active and amorphous form to give rise to such a difference between the energy of activation and the heat of reaction[7].

## CONCLUSIONS

Isothermal weight loss studies confirm the general stoichiometry previously proposed for the thermal decomposition of an aqueous solution of manganese(II) nitrate.

The loss of water from the solution follows a first order rate law as would be expected for either surface vaporization of bulk diffusion as the rate determining step. The energy of activation is 6–10 kcal/mole depending upon the atmosphere and the preexponential term is very small because of the limited surface available for reaction.

The decomposition of the anhydrous manganese nitrate seems to follow an Erofeev equation with $n = 4$ best. The activation energy, 20–25 kcal/mole, is not very dependent upon the choice of atmosphere.

The decomposition of the intermediate manganese(III) oxide follows a number of different rate expressions reasonably well but the contracting area equation seems to be generally the best. It displays a very marked dependence upon the ambient moisture content. The activation energy is lowered about 12 kcal/mole by moisture but the surface area and hence the preexponential term is also decreased. These conflicting effects lead to a crossover in relative rates at about 190°C.

Finally the manganese(IV) oxide dissociates to manganese(III) oxide according to $kt = [1-(1-\alpha)^{\frac{1}{3}}]^{\frac{1}{2}}$. The activation energy is 47–57 kcal/mole depending upon the atmosphere. Moisture again tends to reduce the activation energy and preexponential term. The heat of reaction is only +19 kcal/mole which implies that the resulting manganese(III) oxide is in a highly active or disorganized state.

In those cases where several rate expressions appear to fit the experimental data, the activation energy is essentially independent of the equation selected.

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