polyacetate (Sepraphore, Gelman) at 190 V and pH 10.8 in a Gelman Model 51100 chamber indicated a neutral product and a cationic reactant. A boric acid–NaOH buffer solution was used.

Acknowledgment. The authors wish to express their appreciation for the support of this research through National Science Foundation Grants No. GP-8304 and GP-20275. A matching fund grant by the National Science Foundation to the Department of Chemistry for the spectropolarimeter used in this study is also gratefully acknowledged. Discussions with O. E. Weigang, W. 'A. Baker, P. Krumholz, V. M. Maganian, J. O. Edwards, and J. C. Bailar, Jr., concerning this work have also been extremely helpful. Constructive cirticism by the referees is also acknowledged.

Chemistry and Kinetics of the Thermal Decomposition of Zinc and Magnesium Oxalates

Joseph D. Danforth* and James Dix

Contribution from the Chemistry Department, Grinnell College, Grinnell, Iowa 50112. *Received March 29, 1971*

Abstract: The thermal decompositions of magnesium and zinc oxalates have been studied by a technique which allows the independent and quantitative measurements of carbon monoxide and carbon dioxide formed during 2-min intervals throughout a decomposition. From these measurements, the average rate of decomposition during any interval and the fraction decomposed at any time can be calculated. An equation was found to represent the kinetic data for the decomposition of both oxalates. This equation, $d\alpha/dt = k_1(1-\alpha) + k_2\alpha(1-\alpha)$, has relevant interpretations in terms of the kinetics of the decompositions. Thus, the term $k_1(1-\alpha)$ can be considered to represent a thermal decomposition path (negligible for zinc oxalate), while the term $k_2\alpha(1-\alpha)$ may be considered as representing a path that is accelerated by the oxide formed during the decomposition. This equation can be used to correctly predict the values of the fraction decomposed at which the maximum rate will be observed. A single activation energy was obtained from Arrhenius plots of rate constants. A reasonable decomposition mechanism has been suggested on the basis of the common activation energy and the kinetic behavior.

In this paper we report the results of experiments on the kinetics and stoichiometry of the thermal decompositions of zinc and magnesium oxalates. Rates of formation of carbon dioxide and carbon monoxide were independently and quantitatively determined. Yankwich and Zavitsanos[1] reported kinetic data for these decompositions that were based on the observed pressures of the gaseous products during the decomposition. Giovanoli and Wiedemann[2] have shown that water is present in zinc oxalate even after drying, and that this water caused the conversion of carbon monoxide to carbon dioxide and hydrogen. This reaction was especially significant during the early phases of the decomposition. When gas pressures were used to obtain values of the fraction decomposed, rates of decomposition would appear to be higher, initially, and the maximum rate would be attained at lower values of the fraction decomposed. In our studies, the independent and quantitative measurements of carbon dioxide and carbon monoxide made it possible to obtain values of the fraction decomposed and the value of the fraction decomposed at which the rate was a maximum that were not in error due to the reaction with water.

The equation $d\alpha/dt = k_1(1-\alpha) + k_2\alpha(1-\alpha)$ represented our data over larger ranges of decomposition than did any of the equations used by Yankwich and Zavitsanos in the correlation of their data for the same decompositions.[1]

Experimental Section

Materials. Zinc oxalate and magnesium oxalate dihydrate were prepared by the methods of Yankwich and Zavitsanos.[1]

Apparatus and Techniques. The apparatus and some of the techniques have been previously described.[3–5] A 25-mg sample of the oxalate dihydrate was charged to the sample chamber and was dehydrated at 180–200° for 1.5–2 hr in flowing helium. The amount of water removed was approximately the theoretical quantity, although for each substance residual small amounts of water remained. The residual water was not removed by longer dehydration times or by evacuation for 24 hr at 200°.

After dehydration, the temperature of the chamber was raised to the temperature of the run. Volatile decomposition products were trapped in the sample chamber while helium carrier gas flowed through the by-pass chamber. In these studies the carrier gas was routed to the sample chamber for 30 sec to pick up volatile products and sweep them into a chromatographic column. Gas flow was then diverted to the by-pass chamber for 90 sec, then back to the sample chamber for 30 sec, and so on for the duration of the run. The chromatographic column was one that separated the carbon monoxide and carbon dioxide into distinct peaks.

From the peak areas of carbon monoxide and carbon dioxide which were measured by an integrator, the fraction decomposed, α, at each sample time was calculated by conventional procedures. The rate, $\Delta\alpha/\Delta t$, was calculated for each sample interval. At the beginning of a run the mole ratio of carbon dioxide to carbon monoxide was as high as three because of the conversion of carbon monoxide to carbon dioxide by reaction with water. This ratio decreased during a run but never attained the theoretical ratio of one. Hydrogen formed by the reaction of carbon monoxide with

---

(1) (a) P. E. Yankwich and P. D. Zavitsanos, *J. Phys. Chem.*, **68**, 457 (1964); (b) *ibid.*, **68**, 1275 (1964); (c) *ibid.*, **69**, 442 (1965); (d) *ibid.*, **69**, 918 (1965).

(2) R. Giovanoli and H. G. Wiedemann, *Helv. Chim. Acta*, **51**, 1134 (1968).

(3) J. D. Danforth and J. H. Roberts, *J. Catal.*, **10**, 252 (1968).

(4) J. D. Danforth, U. S. Patent 3,431,077 (March 4, 1969).

(5) J. D. Danforth and J. Dix, *Inorg. Chem.*, **10**, 1623 (1971).

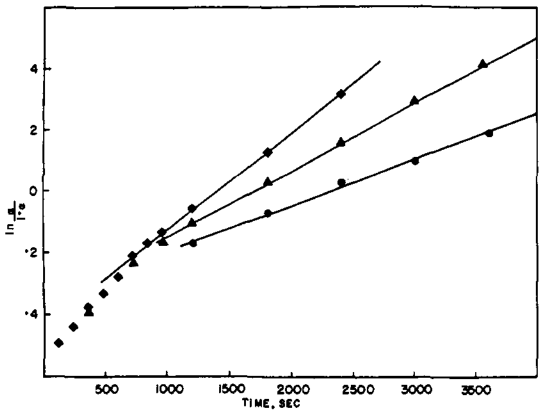

Figure 1. Plots of ln $\alpha/(1 - \alpha)$ *vs.* time for representative runs of zinc oxalate: ●, 435°; ▲, 439.5°; ◆ 460°.

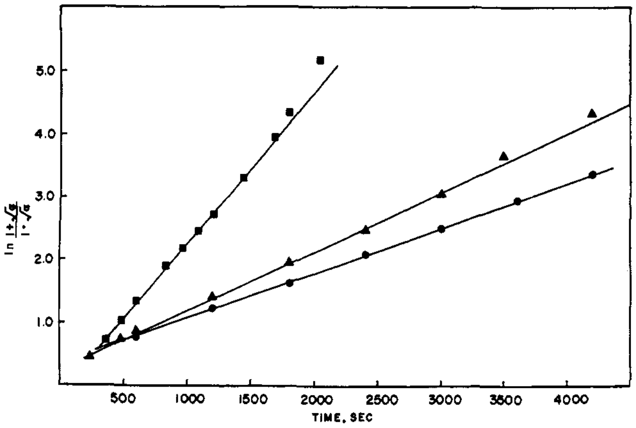

Figure 2. Plots of ln $(1 + \sqrt{\alpha})/(1 - \sqrt{\alpha})$ *vs.* time for representative runs of magnesium oxalate: ●, 352°; ▲, 360°; ■, 366°.

water was not observed in standard runs using helium carrier gas, but it was observed in the amounts expected when carbon monoxide was used as the carrier gas.

It can be shown that the fraction decomposed at any time is represented by the cumulative moles of carbon dioxide plus carbon monoxide divided by the total moles of these gases formed during the run. The values of α obtained from the direct observation of carbon dioxide and carbon monoxide were not in error because of the reaction of carbon monoxide with water.

Results

Zinc oxalate decompositions at various temperatures were represented over ranges of α from 0.2 to 0.9 by the differential equation $d\alpha/dt = k_{Zn}\alpha(1 - \alpha)$. In the integrated form, this equation is $\ln \alpha/(1 - \alpha) = k_{Zn}t + C$. Plots of $\ln \alpha/(1 - \alpha)$ *vs.* t were made and values of k_{Zn} were obtained from the slopes of lines in the range where the kinetic equation held. Representative plots are shown in Figure 1 and the data are summarized in Table I.

Magnesium oxalate decompositions at various temperatures were represented over ranges of α from 0.1 to 0.9 by the differential equation $d\alpha/dt = k_{Mg}\alpha^{1/2}(1 - \alpha)$. In the integrated form, this equation becomes $\ln (1 + \sqrt{\alpha})/(1 - \sqrt{\alpha}) = k_{Mg}t + C$. Plots of $\ln (1 + \sqrt{\alpha})/(1 - \sqrt{\alpha})$ *vs.* t were made and values of k_{Mg} were obtained from the slopes of lines in the range where the kinetic equation held. Representative plots are shown in Figure 2. It was suggested by Gordon[6] that the differential equation representing the decomposition of magnesium oxalate could be represented over large ranges of α by the equation $d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$ when k_1 was 20–80% of $k_1 + k_2$. Thus, $k_{Mg}\alpha^{1/2}(1 - \alpha) = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$; by factoring, $k_{Mg}\alpha^{1/2} = k_1 + k_2\alpha$. Plots of the experimental values of $k_{Mg}\alpha^{1/2}$ *vs.* α gave straight lines of slopes k_2 and intercepts k_1. Representative plots are shown in Figure 3 and values of k_{Mg}, k_1, and k_2 are summarized in Table II.

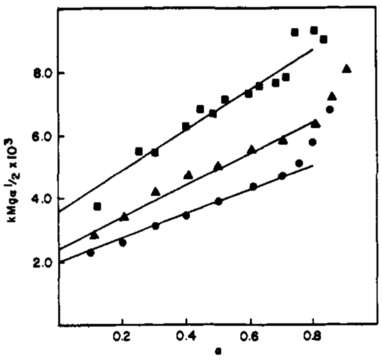

Figure 3. Representative plots of $k_{Mg}\alpha^{1/2}$ *vs.* α for magnesium oxalate: ●, 430°; ▲, 435; ■, 443°.

Table I. Summary of k_{Zn}, Temperature, and Range of Fraction Decomposed over Which the Kinetic Equation $d\alpha/dt = k_{Zn}\alpha(1 - \alpha)$ Holds for Zinc Oxalate

Temp, °C	$k_{Zn} \times 10^3$, sec^{-1}	α
347	1.38	0.12–0.98
352	1.44	0.18–0.95
355	1.59	0.27–0.95
356	1.61	0.16–0.96
360	2.17	0.21–0.97
362.5	2.66	0.14–0.96
366	3.14	0.15–0.96
372.5	5.94	0.15–0.98

Table II. Summary of k_{Mg}, Temperature, and Range of Fraction Decomposed over Which the Kinetic Equation $d\alpha/dt = k_{Mg}\alpha^{1/2}(1 - \alpha)$ Holds for Magnesium Oxalate and Values of k_1 and k_2 from Plots of $k_{Mg}\alpha^{1/2}$ *vs.* α

Temp, °C	$k_{Mg} \times 10^3$, sec^{-1}	α	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^4$, sec^{-1}
430	0.57	0.10–0.90	2.0	4.0
435	0.70	0.13–0.90	2.4	5.2
439.5	0.94	0.08–0.90	3.2	6.7
443	0.99	0.11–0.92	3.5	7.0
449	1.46	0.05–0.94	5.2	10.0
460	2.33	0.06–0.70	8.2	16.0

From the differential equation $d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$, the relationship $d\alpha/dt(1 - \alpha)^{-1} = k_1 + k_2\alpha$ is obtained. At the lowest temperatures the observed rate, $\Delta\alpha/\Delta t$, approached $d\alpha/dt$. Plots of $(\Delta\alpha/\Delta t)(1 - \alpha)^{-1}$ *vs.* α are shown in Figure 4 for low-temperature runs of zinc and magnesium oxalates. The value of k_1 for zinc oxalate is approximately zero and the values of k_1 and k_2 for magnesium oxalate are the same as those obtained by the other method and reported in Table II. At higher temperatures, decom-

---

(6) G. Gordon, The State University of Iowa, personal communication, 1970.

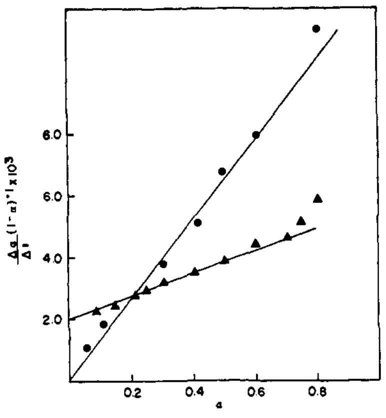

Figure 4. Plots of $(\Delta\alpha/\Delta t)(1 - \alpha)^{-1}$ *vs.* α: ●, zinc oxalate at 347°; ▲, magnesium oxalate at 430°.

position rates were greater and $\Delta\alpha/\Delta t$ did not approach $d\alpha/dt$. Under these conditions, experimental values of $k_{Mg}\alpha^{1/2}$ were used to evaluate k_1 and k_2.

Arrhenius activation energies and frequency factors recorded in Table III were obtained from a least-squares analysis of the rate constants and temperatures reported in Tables I and II.

Table III. Arrhenius Activation Energies and Frequency Factors

Rate constant	Activation energy, kcal/mol	Frequency factor[a]
k_{Zn}	47 ± 6	3×10^{13}
k_{Mg}	48 ± 2	4×10^{11}
k_1	49 ± 2	3×10^{11}
k_2	47 ± 2	1×10^{11}

[a] Standard deviations associated with the activation energies are not simple ± deviations. The range of the frequency factor for k_{Zn} is from 3×10^{11} to 9×10^{15} because of the large standard deviation in the activation energy. Values for k_{Mg}, k_1, and k_2 are better. Thus, the frequency factor for k_{Mg} lies between 1×10^{11} and 18×10^{11}, with a probable value of 4×10^{11}.

A single activation energy of approximately 48 kcal/mol can be assigned for the decomposition of magnesium oxalate by either the thermal path (using k_1) or the accelerated path (using k_2).

Even though the standard deviation of the activation energy of zinc oxalate is large, it seems reasonable to suggest that its activation energy is the same or very nearly the same as that for magnesium oxalate. Supporting this suggestion are activation energies of zinc oxalate decomposition reported by Yankwich and Zavitsanos.[1] These are: for the "power of *t*" relation, 49 ± 2; for the "contracting sphere" equation, 53 ± 5; for the "rate law of order *n*," 51 ± 2; and for the "Avrami" equation, 48 ± 3. Thus, it appears that zinc oxalate and magnesium oxalate have the same activation energies and that the activation energies for the thermal and accelerated pathways of magnesium oxalate have this same value.

The kinetic equation can be used to predict the value of the fraction decomposed at which the maximum rate occurs. Thus, when the derivative of the rate with respect to α is taken and this value is set equal to zero, the value of the fraction decomposed at which the maximum rate is expected can be expressed as

$$\alpha_{\text{max rate}} = (k_2 - k_1)/2k_2$$

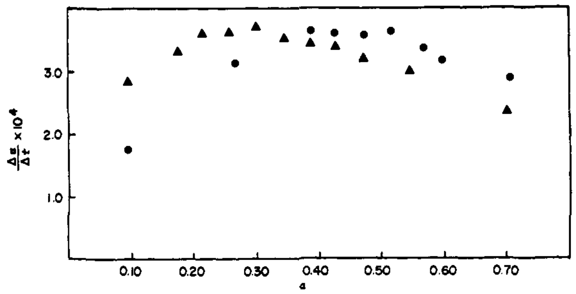

Figure 5. Representative plots of rate, $\Delta\alpha/\Delta t$, *vs.* α: ●, zinc oxalate at 352°; ▲, magnesium oxalate at 439.5°.

When k_1 is negligible, the maximum rate is predicted to appear at 0.5α. The plots of $\Delta\alpha/\Delta t$ as a function of α shown in Figure 5 illustrate that this prediction is fulfilled for the decomposition of zinc oxalate.

From the rate constants of Table II it was calculated that the maximum rate for magnesium oxalate should appear at 0.24α–0.27α. The plot for magnesium oxalate in Figure 5 shows the maximum rate near this calculated range of α. Although only one example of each decomposition has been illustrated, plots of all runs consistently showed that the maximum rates were attained near the predicted values of α.

On the basis of the behavior of zinc and magnesium oxalates, it would be expected that calcium oxalate which decomposed at still higher temperatures should attain its maximum rate of decomposition at smaller values of α. It has been reported that calcium oxalate attains its maximum rate of decomposition in the region of 0.05α–0.10α.[7]

Discussion

A new kinetic equation, $d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$ has been found to represent the decompositions of zinc and magnesium oxalates over large ranges of the fraction decomposed. The term $k_1(1 - \alpha)$ has been interpreted as representing a thermal decomposition on the surface of the solid. The second term has been interpreted as representing a pathway that is accelerated by the presence of the decomposition product. A single activation energy of approximately 48 kcal/mol for both decompositions and for the two paths of the magnesium oxalate decomposition is interpreted to mean that there is a common rate-controlling activation step. We suggest that this activation step is the formation of a radical ion, $C_2O_4^-$, by the transfer of an electron from an oxalate ion to a metal orbital. This is the same as the activation step suggested for photochemical activation of an oxalate by Parker and Hatchard.[8] Once activated, the radical ion moves rapidly to the surface by electron exchange with oxalate ions. In other terminology, this is equivalent to saying that there is a movement of a positive hole to the surface. The electron freed in the formation of the radical ion moves to the surface as a negative hole. At the surface, the active species decomposes by either the thermal path or the path that is ac-

---

(7) F. E. Freeberg, K. O. Hartman, I. C. Histatsune, and J. M. Schempf, *J. Phys. Chem.*, 71, 399 (1967).

(8) C. A. Parker and C. G. Hatchard, *ibid.*, 63, 22 (1959).

celerated, but neither path is rate controlling. The idea of thermal and catalytic pathways is not unusual. A similar approach has been proposed for correlating the kinetics of the hydrolysis of esters.[9]

For zinc oxalate decompositions which occur in the temperature range 347–372.5°, the product, zinc oxide, is considered to be strongly acceleratory. In this temperature range, the thermal decomposition is negligible and the correlating equation assumes the differential form of the Prout–Tompkins equation,[10] $d\alpha/dt = k\alpha(1 - \alpha)$.

Silver oxide follows similar kinetics; this was interpreted by Hood and Murphy in terms of the catalytic effect of the silver formed during the decomposition.[11] In our mechanism, we have preferred to use the term acceleratory effect, because there is no lowering of the activation energy due to the presence of the decomposition product.

Magnesium oxalate decompositions occurred in the temperature range from 430 to 460°. The higher temperature of decomposition may be attributed to a lower acceleratory effect of the magnesium oxide. In this temperature range, decomposition by the thermal pathway becomes significant and both terms must be considered in representing our kinetic data.

In addition to being compatible with a rational and simple mechanism of decomposition, the proposed equation may be used for the prediction of the fraction decomposed at which the maximum rate will be observed. As has been pointed out, the predicted values are reasonably close to the maxima shown in Figure 5 for representative decompositions of the two substances. The oxalate decompositions appear to represent a simple example in which the thermal and acceleratory decompositions are first order with respect to decomposing oxalate. If this approach to the kinetic analysis of solid decompositions is more generally applicable, it can be expected that examples may be found which represent second-order dependence on the decomposing substance.

Acknowledgments. This research was supported by the National Science Foundation. A Sloan Grant to Grinnell College gave released time to one of the authors for the more effective conducting of this research.

---

(9) M. Boudart, "Kinetics of Chemical Processes," Prentice-Hall, Englewood Cliffs, N. J., 1968, p 125.

(10) D. A. Young in "The International Encyclopedia of Physical Chemistry and Chemical Physics," Pergamon Press, Elmsford, N. Y., 1966, pp 49–51.

(11) G. C. Hood, Jr., and G. W. Murphy, *J. Chem. Educ.*, **26**, 169 (1949).