

EVALUATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC TRACES

PART II. THERMAL DEHYDROXYLATION OF $Mg(OH)_2$

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ABSTRACT

A combined numerical method was employed to treat the thermogravimetric data for the dehydroxylation of magnesium hydroxide obtained in our own laboratory. Satisfactory results were obtained. The data were also treated with Freeman and Carroll's, Coats and Redfern's and Satava's method. The agreement between the results obtained by the present method and those of Coats and Redfern's and Satava's method were also satisfactory.

INTRODUCTION

In part I of this paper¹, a combined numerical method was proposed to evaluate kinetic parameters from thermogravimetric data. The method has proved to be satisfactory using a set of artificial data and the data of dehydration of gypsum by Šesták et al.² In this paper, the proposed method is applied to evaluate kinetic parameters for the thermal dehydroxylation of $Mg(OH)_2$.

EXPERIMENTAL PART

0.05 mol of magnesium chloride was dissolved in 100 ml CO_2 free distilled water. Equivalent amounts of 0.5 M ammonium hydroxide solution were slowly added to precipitate all the magnesium ions. The mixture was kept in a glass-stoppered bottle and allowed to stand for one week with occasional shaking. The magnesium hydroxide precipitate was separated from the mother liquid by centrifugation and washed free from chloride. The precipitate was then dried at 80°C and pulverized to pass through a 100-mesh sieve.

Approximately 15 mg of the prepared $Mg(OH)_2$ were weighed in an aluminum pan and covered with a lid, without being pressed. $\alpha-Al_2O_3$ was used as the reference sample. Both the sample and reference sample were placed in a desk-top differential scanning calorimeter and thermogravimetric analyzer manufactured by Rigaku Denki Co. Ltd., Japan. Experimental conditions were as follows: heating rate, 5°C min^{-1} ; DSC range ± 8 m cal sec^{-1} ; chart speed, 5 mm min^{-1} ; temperature full scale, 20 mV; TG range, 10 mg; DTG sensitivity, 0.2 division.

RESULTS

Duplicate data curves were taken for each sample. One of them is reproduced in Fig. 1. The curve ABC represents the TG curve, the curve DEF, the DSC curve; the curve IJK, the DTG curve and the line GH, the temperature of the sample. The instrument has a three pen recorder. One pen records both TG and DTG data; it records DTG continuously while TG data are recorded intermittently. The line AL represents the baseline of the TG curve. It was drawn manually by inspection of the initial part of the TG data. Weight changes, ΔW , were read from the differences between TG curve and the baseline. Twenty-one points were taken. Their ΔW values are listed in Table 1, together with the corresponding temperatures in centigrade. Temperatures were read from the line GH, using a special ruler supplied by the manufacturer. The scale of the ruler varies in accordance to the value of temperature

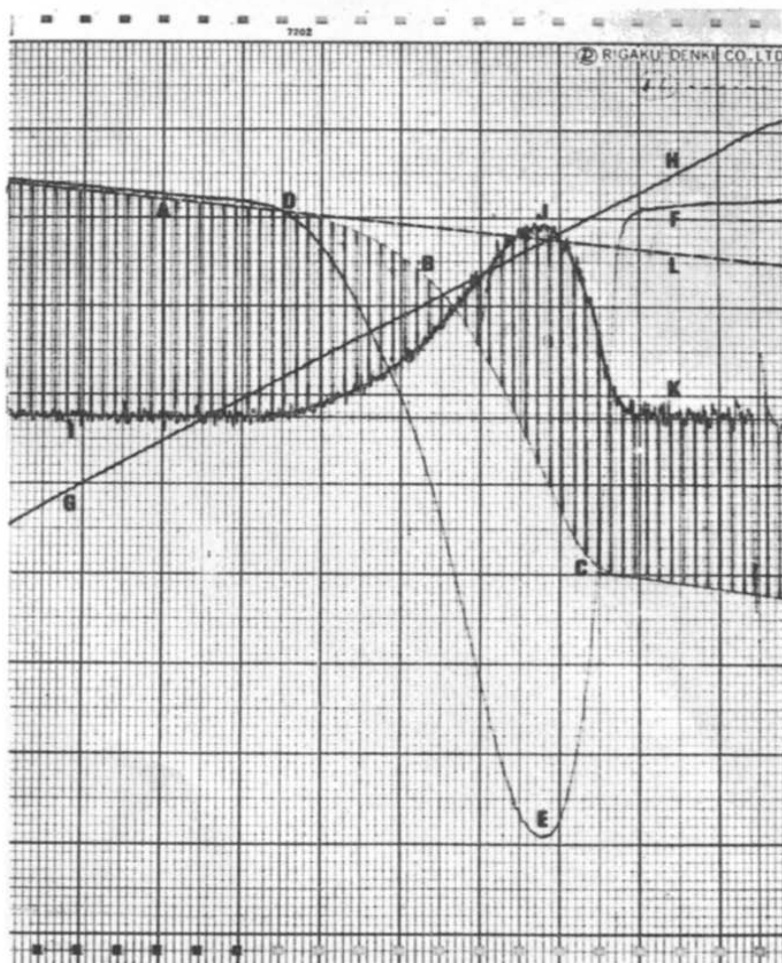


Fig. 1. Simultaneous TG-DTG-DSC of $Mg(OH)_2$.

TABLE 1
THERMAL DEHYDROXYLATION OF $Mg(OH)_2$

Data point	Trace 1 ($W_0 = 14.22$ mg)		Trace 2 ($W_0 = 14.12$ mg)	
	t ($^{\circ}C$)	ΔW (mg)	t ($^{\circ}C$)	ΔW (mg)
1	345	0.11	343	0.10
2	349	0.15	346	0.12
3	352	0.21	349	0.15
4	355	0.26	352	0.23
5	359	0.35	356	0.27
6	362	0.42	359	0.34
7	365	0.51	362	0.46
8	368	0.63	365	0.56
9	372	0.78	369	0.69
10	375	0.94	372	0.85
11	379	1.15	375	0.96
12	381	1.31	378	1.16
13	384	1.53	381	1.38
14	387	1.80	385	1.64
15	391	2.07	388	1.87
16	394	2.33	391	2.17
17	397	2.59	394	2.41
18	401	2.87	397	2.68
19	404	3.12	401	2.96
20	407	3.32	404	3.18
21	411	3.49	408	3.36

full scale set on the instrument. The fraction of conversion, α values, were calculated from ΔW and the theoretical total weight loss because the dehydroxylation reaction is only completed up to $1000^{\circ}C^3$. They are listed in Table 2 together with the corresponding absolute temperature, and are plotted in Fig. 2. The DTG sensitivity employed in the present experiments is the second highest of the instrument. Very large noise was observed. If the sensitivity were reduced, the noise could also be reduced, but the accuracy would not be high enough. Therefore, the DTG data were not taken to calculate the rate of reaction. Instead, dx/dT values were obtained using the curve fitting method. By means of a least squares fit, α values were approximated by a polynomial in T with six degrees. The coefficients obtained are shown in Table 3. From these polynomials, dx/dT values were obtained. They are also listed in Table 2.

Results from the LLS method are shown in Tables 4 and 5 for traces 1 and 2, respectively. It is seen from Table 4 that, the only possible mechanism for the thermal dehydroxylation of $Mg(OH)_2$ is of n type, because the obtained parameters for other types of mechanism are unreasonable. From this table, n is found to be 1.656; E , 55.623 kcal mol $^{-1}$ and A , 9.005×10^{15} sec $^{-1}$. Inspection of Table 5 shows that, parameters for the types n , $n-m$ and $n-p$ are all reasonable. For the $n-m$ type of mechanism, the value of m is 0.0003 which could be neglected. The value of p for the $n-p$ type of mechanism is also small enough to be neglected. These results also lead to the n type of mechanism with values of n , E and A being 1.518, 52.646 kcal mol $^{-1}$

and $9.206 \times 10^{14} \text{ sec}^{-1}$, respectively. These values were further treated by the differential correction method; results are shown in Tables 6 and 7. It is seen that the values of n , A and E vary as the iterating procedure proceeds. The values become consistent after ten counts. The resultant kinetic parameters are shown in Table 8: $f(\alpha) = (1-\alpha)^{1.6}$, $E = 53.0 \text{ kcal mol}^{-1}$, $A = 1.2 \times 10^{15} \text{ sec}^{-1}$ for trace 1 and $f(\alpha) = (1-\alpha)^{1.6}$, $E = 53.4 \text{ kcal mol}^{-1}$, $A = 1.6 \times 10^{15} \text{ sec}^{-1}$ for trace 2. It is interesting to

TABLE 2

 α AND $T(K)$ VALUES FROM TG TRACES

Data point	Trace 1			Trace 2		
	$T(K)$	α	$\frac{d\alpha}{dT} (10^{-2} \text{ sec}^{-1})$	$T(K)$	α	$\frac{d\alpha}{dT} (10^{-2} \text{ sec}^{-1})$
1	618	0.0251	—	616	0.0229	—
2	622	0.0342	—	619	0.0275	—
3	625	0.0478	0.390	622	0.0344	0.336
4	628	0.0592	0.443	625	0.0528	0.427
5	632	0.0797	0.532	629	0.0619	0.527
6	635	0.0957	0.622	632	0.0780	0.603
7	638	0.1162	0.736	635	0.1055	0.690
8	641	0.1435	0.871	638	0.1284	0.793
9	645	0.1777	1.077	642	0.1583	0.958
10	648	0.2141	1.243	645	0.1950	1.103
11	652	0.2620	1.462	648	0.2202	1.261
12	654	0.2894	1.565	651	0.2661	1.426
13	657	0.3485	1.703	654	0.3165	1.590
14	660	0.4100	1.812	658	0.3762	1.787
15	664	0.4715	1.897	661	0.4289	1.902
16	667	0.5308	1.905	664	0.4977	1.972
17	670	0.5900	1.859	667	0.5528	1.982
18	674	0.6538	1.710	670	0.6147	1.914
19	677	0.7107	1.533	674	0.6789	1.668
20	680	0.7563	1.305	677	0.7294	1.342
21	684	0.7950	—	681	0.7706	—

TABLE 3

COEFFICIENTS FROM LEAST SQUARE POLYNOMIAL FIT

$$(\alpha = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 + a_6 T^5 + a_7 T^6)$$

Coefficient	Trace 1	Trace 2
a_1	2.389401204×10^6	9.954967668×10^5
a_2	-2.202207920×10^4	-8.872998466×10^3
a_3	84.51069348	32.85288143
a_4	-0.1728425922	-0.064657325544
a_5	$1.986969955 \times 10^{-4}$	$7.131186862 \times 10^{-5}$
a_6	$-1.217311364 \times 10^{-7}$	$-4.177218115 \times 10^{-8}$
a_7	$3.105022441 \times 10^{-11}$	$1.014733674 \times 10^{-11}$

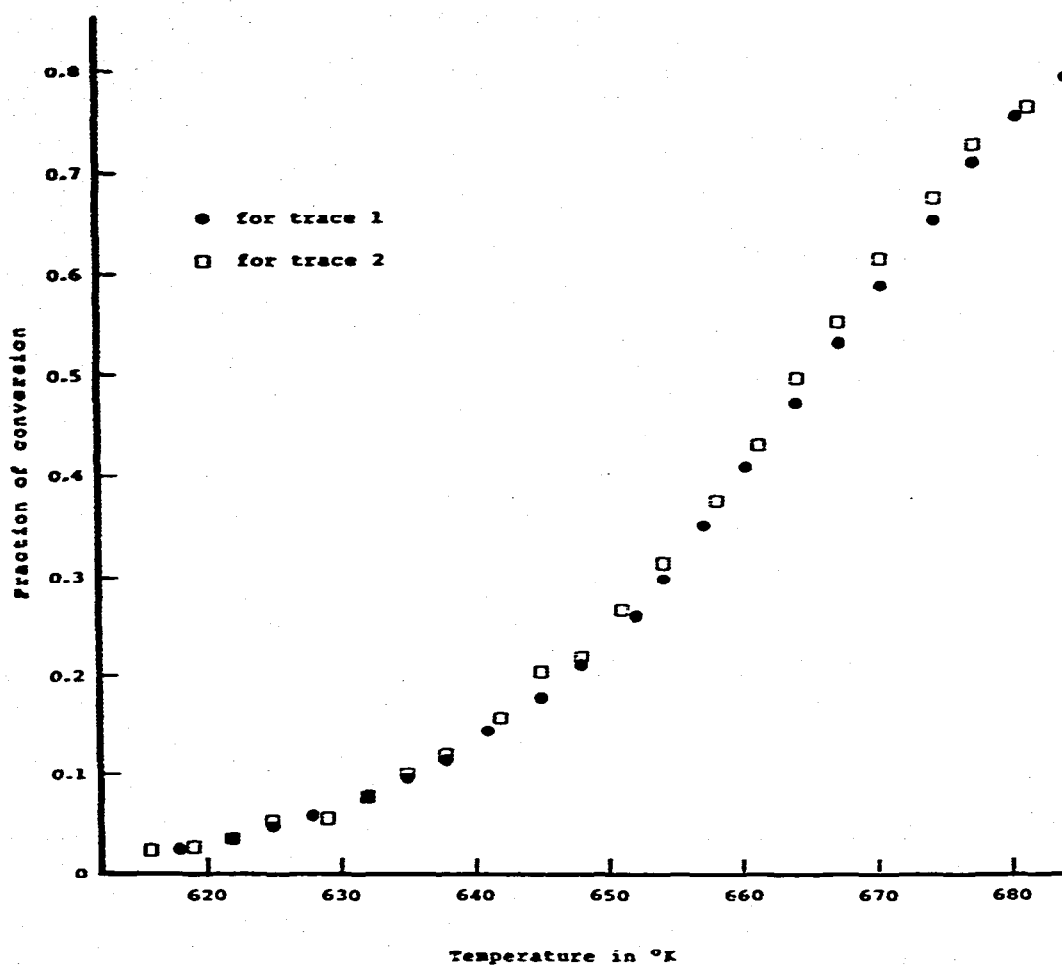


Fig. 2. Fraction of conversion at various temperatures for thermal dehydroxylation of $\text{Mg}(\text{OH})_2$.

TABLE 4
RESULTS FROM THE LLS PROCEDURE FOR TRACE 1

$f(x)$	A (sec^{-1})	E (kcal mol^{-1})	n	m	p
$(1-\alpha)^p$	9.005×10^{15}	55.623	1.656		
α^m	1.157×10^{-27}	-75.542		2.281	
$[(-\ln(1-\alpha))^p]$	$< 10^{-78}$	-232.960			4.916
$(1-\alpha)^m \alpha^n$	1.347×10^6	25.570	1.281	0.525	
$(1-\alpha)^m [-\ln(1-\alpha)]^p$	0.532	6.027	1.397		0.855

TABLE 5

RESULTS FROM THE LLS PROCEDURE FOR TRACE 2

$f(x)$	A (sec^{-1})	E (kcal mol^{-1})	n	m	p
$(1-\alpha)^n$	9.206×10^{14}	52.646	1.518		
α^n	6.180×10^{-19}	-48.240		1.609	
$[-\ln(1-\alpha)]^p$	2.316×10^{-35}	-97.777			2.284
$(1-\alpha)^n \alpha^m$	9.094×10^{14}	52.630	1.518	0.0003	
$(1-\alpha)^n [-\ln(1-\alpha)]^p$	4.582×10^{13}	48.677	1.493		0.065

TABLE 6

RESULTS FROM THE DC PROCEDURE FOR TRACE 1

Final $\Delta n = 1.9 \times 10^{-6}$; final $\Delta A = 3.4 \times 10^{10}$; final $\Delta E = 3.6 \times 10^{-2}$.

Count	n	A (10^{15} sec^{-1})	E (kcal mol^{-1})
0	1.6555	9.0048	55.623
1	1.5581	-14.479	52.289
2	1.5863	1.0554	52.245
3	1.6083	1.3088	53.050
4	1.6033	1.5402	53.370
5	1.5897	1.1992	53.076
6	1.5876	1.2024	53.043
7	1.5869	1.1886	53.029
8	1.5867	1.1857	53.026
9	1.5867	1.1850	53.025
10	1.5867	1.1848	53.025
11	1.5867	1.1848	53.025

TABLE 7

RESULTS FROM THE DC PROCEDURE FOR TRACE 2

Final $\Delta n = 4.0 \times 10^{-6}$; final $\Delta A = 9.6 \times 10^{10}$; final $\Delta E = 7.4 \times 10^{-2}$.

Count	n	A (10^{15} sec^{-1})	E (kcal mol^{-1})
0	1.5178	0.9206	52.646
1	1.5411	0.8372	52.531
2	1.5722	1.2695	53.174
3	1.5789	1.5275	53.296
4	1.5811	1.5825	53.325
5	1.5822	1.6119	53.347
6	1.5826	1.6198	53.353
7	1.5827	1.6227	53.355
8	1.5827	1.6235	53.356
9	1.5827	1.6238	53.356
10	1.5827	1.6239	53.356

TABLE 8
KINETIC PARAMETERS OBTAINED BY VARIOUS METHODS FOR THE THERMAL DEHYDROXYLATION OF $Mg(OH)_2$

Computing method	Trace 1		Trace 2		Average				
	n	E (kcal mol ⁻¹)	A (sec ⁻¹)	n	E (kcal mol ⁻¹)	A (sec ⁻¹)	n	E (kcal mol ⁻¹)	A (sec ⁻¹)
Freeman and Cirroll	1.7	57.2	3.7×10^{17}	1.5	53.0	1.4×10^{16}	1.6	55.1	7.2×10^{16}
Couts and Redfern	1.5	55.3	3.7×10^{15}	1.5	56.3	9.1×10^{15}	1.5	55.8	5.8×10^{15}
Sitovii	1.5	55.5	3.8×10^{15}	1.5	56.6	9.5×10^{15}	1.5	56.0	6.0×10^{15}
Present method	1.6	53.0	1.2×10^{15}	1.6	53.4	1.6×10^{15}	1.6	53.2	1.4×10^{15}

note that, although the values of A obtained with the LLS method differ from each other by one order of magnitude for the two traces, the values obtained by further DC treatment are very close to each other. A further point to note is that, the value of A in Table 6 passed through a negative value at which the error is a maximum. A repeated computing procedure gave the same result.

For comparison, the above data were also treated by several other accepted methods namely, Freeman and Carroll's, Coats and Redfern's and Satava's method.

(a) *Freeman and Carroll's treatment*

According to Freeman and Carroll⁴, a plot of $\Delta \ln (dx/dT)/\Delta \ln (1-x)$ against $\Delta(1/T)/\Delta \ln (1-x)$ should yield a straight line, the slope gives E/R and the intercept at the Y-axis gives the value of n . Nine data points were taken for calculation and $f(x)$ was assumed to be $(1-x)^n$. Results are listed in Table 9 and plotted in Fig. 3. The resultant parameters are also shown in Table 8. It is seen that $f(x) = (1-x)^{1.7}$, $A = 3.7 \times 10^{17} \text{ sec}^{-1}$, $E = 57.2 \text{ kcal mol}^{-1}$ for trace 1 and $f(x) = (1-x)^{1.5}$, $A = 1.4 \times 10^{16} \text{ sec}^{-1}$, $E = 53.0 \text{ kcal mol}^{-1}$ for trace 2. The agreement is not good.

(b) *Coats and Redfern's treatment*

According to these authors⁵, a plot of $\ln [g(x)/T^2]$ against $1/T$ should yield a straight line with a slope of $-E/R$, if $g(x)$ is the correct function, where $g(x)$ is defined by the following equation

$$g(x) = \int_0^x \frac{dx}{f(x)} \quad (1)$$

Seventeen $g(x)$ forms were used in the trial and error procedure. They are mainly taken from Gallagher and Johnson⁶, and are listed in Table 10, together with their corresponding forms of $f(x)$. It can be seen that these seventeen forms of $g(x)$ can all be included in the five types of mechanism given by Šesták and Berggren⁷ which are employed in the present suggested method. The results of the trial and error procedure by Coats and Redfern's treatment are shown in Tables 11 and 12. The linearities of various plots are represented by their correlation coefficients. Correlation coefficient of unity indicates a perfect straight line. It is seen that, there are several forms of $g(x)$ which have approximately the same correlation coefficients. Among these, functions 16 and 17 give the highest linearity. The latter function was not given by Gallagher and Johnson⁶. However, function 16 yields kinetic parameters higher than those obtained by the present method. Judging from the trend of functions 6, 7, 8 and 16, the magnitude of kinetic parameters increases as the exponential of the $f(x)$ form increases. Function 17 was, then, proposed, which yields kinetic parameters in better agreement with those obtained by the present method. Therefore, the most probable mechanism is $f(x) = (1-x)^{1.5}$. The activation energy and frequency factor are $55.3 \text{ kcal mol}^{-1}$ and $3.7 \times 10^{15} \text{ sec}^{-1}$, respectively for trace 1 and $56.3 \text{ kcal mol}^{-1}$ and $9.1 \times 10^{15} \text{ sec}^{-1}$, respectively for trace 2. These values are also summarized in Table 8. The agreement between the two sets of parameters may be considered as good.

TABLE 9

FREEMAN AND CARROLLS TREATMENT

Data point	Trace 1		Trace 2	
	$\frac{\Delta \ln (dx/dT)}{\Delta \ln (1-\alpha)}$	$\frac{\Delta (1/T)}{\Delta \ln (1-\alpha)}$	$\frac{\Delta \ln (dx/dT)}{\Delta \ln (1-\alpha)}$	$\frac{\Delta (1/T)}{\Delta \ln (1-\alpha)}$
19	reference point		reference point	
17	0.5528	4.425	0.5206	4.699
15	0.3530	4.799	0.2275	5.068
13	0.1292	5.539	-0.0636	6.006
11	-0.0506	6.047	-0.3153	6.709
9	-0.3381	7.015	-0.5752	7.674
7	-0.6572	8.085	-0.8617	8.894
5	-0.9150	9.088	-1.0741	9.901
3	-1.1483	10.316	-1.4541	11.266

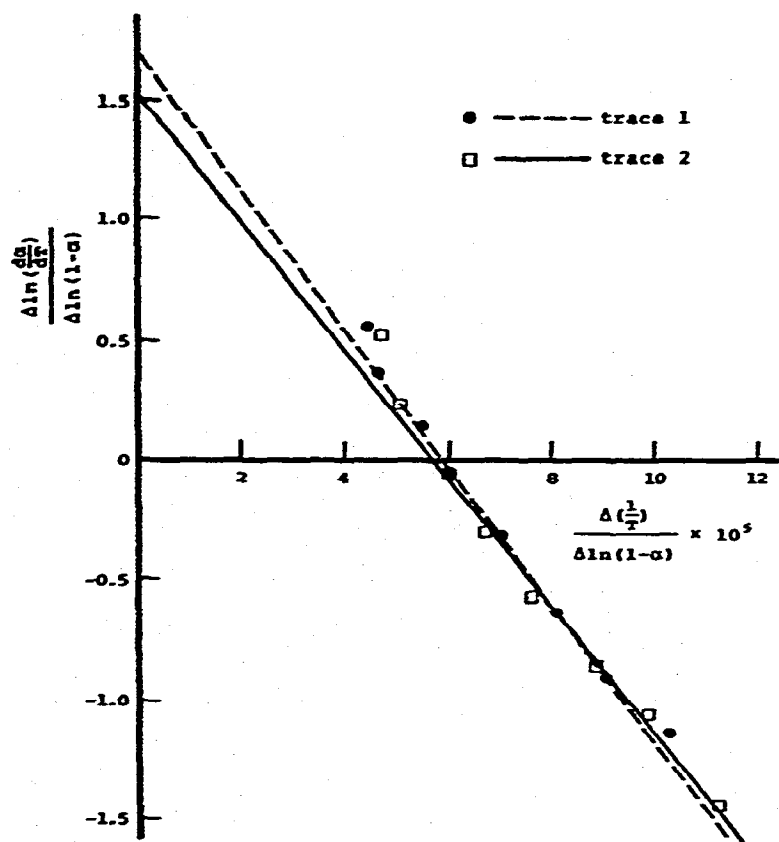
Fig. 3. Freeman-Carroll's plot for thermal dehydroxylation of $Mg(OH)_2$.

TABLE 10

KINETIC FUNCTIONS USED IN THE TRIAL AND ERROR PROCEDURE FOR COATS AND REDFERN'S AND SATAVA'S METHODS

Function No.	$g(\alpha)$	$f(\alpha)$	Name of the mechanism
1	α	α^0	Power law
2	α^2	α^{-1}	
3	$\alpha^{1/2}$	$\alpha^{1/2}$	
4	$\alpha^{1/3}$	$\alpha^{2/3}$	
5	$\alpha^{1/4}$	$\alpha^{3/4}$	
6	$1-(1-\alpha)^{1/2}$	$(1-\alpha)^{1/2}$	Contracting geometry
7	$1-(1-\alpha)^{1/3}$	$(1-\alpha)^{2/3}$	
8	$-\ln(1-\alpha)$	$(1-\alpha)$	
9	$[-\ln(1-\alpha)]^{1/1.5}$	$(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	Erofeev
10	$[-\ln(1-\alpha)]^{1/2}$	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	
11	$[-\ln(1-\alpha)]^{1/3}$	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	
12	$[-\ln(1-\alpha)]^{1/4}$	$(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	
13	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	Diffusion controlled, 2D
14 ^a	$1-2\alpha/3-(1-\alpha)^{2/3}$	$[-\ln(1-\alpha)]^{-1}$	Diffusion controlled, 3D
15 ^a	$[1-(1-\alpha)^{1/3}]^2$	$(1-\alpha)^{1/3}[- \ln(1-\alpha)]^{-1}$	Jander
16	$(1-\alpha)^{-2}-1$	$(1-\alpha)^2$	Second order
17	$(1-\alpha)^{-1/2}-1$	$(1-\alpha)^{1.5}$	One and half order

^a $f(\alpha)$ forms have been approximated by Šesták and Berggren⁷.

TABLE 11

RESULTS FROM COATS AND REDFERN'S METHOD FOR TRACE 1

Function No.	E (kcal mol ⁻¹)	A (sec ⁻¹)	Correlation coefficient
1	41.955	1.2×10^{11}	0.987
2	86.493	5.6×10^{25}	0.988
3	19.686	3.4×10^3	0.985
4	12.263	6.7	0.982
5	8.551	<1	0.980
6	45.900	1.6×10^{12}	0.993
7	47.324	3.5×10^{12}	0.995
8	50.338	1.3×10^{14}	0.997
9	32.698	1.4×10^8	0.997
10	23.878	1.2×10^5	0.997
11	15.157	8.9×10^1	0.997
12	10.645	<1	0.997
13	91.462	1.6×10^{27}	0.991
14	93.374	1.7×10^{27}	0.993
15	97.231	3.9×10^{28}	0.995
16	60.716	6.3×10^{17}	0.999
17	55.281	3.7×10^{13}	0.999

TABLE 12

RESULTS FROM COATS AND REDFERNS METHOD FOR TRACE 2

Function No.	E (kcal mol ⁻¹)	A (sec ⁻¹)	Correlation coefficient
1	44.053	6.9×10^{11}	0.987
2	90.678	1.7×10^{27}	0.988
3	20.741	8.4×10^3	0.986
4	12.970	1.3×10^1	0.984
5	9.084	< 1	0.981
6	47.731	7.3×10^{12}	0.993
7	49.094	1.5×10^{13}	0.994
8	51.826	4.4×10^{14}	0.997
9	33.693	3.2×10^8	0.997
10	24.627	2.4×10^5	0.996
11	15.516	1.4×10^2	0.996
12	11.027	2.6	0.995
13	95.333	3.8×10^{28}	0.992
14	97.104	3.5×10^{28}	0.993
15	100.670	> 10^{30}	0.995
16	61.284	1.1×10^{18}	0.999
17	56.347	9.1×10^{15}	0.999

(c) Satava's treatment

According to Satava⁸, a plot of $\ln g(\alpha)$ against $1/T$ should be a straight line if a correct form of $f(\alpha)$ were chosen. Let s be the slope of the straight line, then the activation energy is given by the following equation

$$E = s + (s^2 + 8s\bar{T})^{1/2} \quad (2)$$

where \bar{T} is the average temperature. The seventeen forms of $g(\alpha)$ used in the trial and error procedure for Coats and Redfern's method were also employed here. The results are shown in Tables 13 and 14. They are very similar and parallel to those obtained with Coats and Redfern's treatment. Again, judging from both the linearity and the frequency factor, it is seen that the most preferable form of $f(\alpha)$ is $(1-\alpha)^{1-5}$. The activation energy and frequency factor are $55.5 \text{ kcal mol}^{-1}$ and $3.8 \times 10^{15} \text{ sec}^{-1}$, respectively for trace 1 and $56.6 \text{ kcal mol}^{-1}$ and $9.5 \times 10^{15} \text{ sec}^{-1}$, respectively for trace 2. These values are also shown in Table 8.

CONCLUSION

From the above results, it is seen that Coats and Redfern's and Satava's method agree with each other very well. However, it is very difficult to determine the right reaction mechanism, because at least half of the $g(\alpha)$ forms tested give correlation coefficients higher than 0.995. Kinetic parameters deduced from Freeman and Carroll's method are somewhat higher than those obtained by other methods. The agreement between the two sets of data is poor. The present method gives the lowest E and A values. The value of n obtained by the present method is in between the values

TABLE 13

RESULTS FROM SATAVA'S METHOD FOR TRACE 1

Function No.	E (kcal mol ⁻¹)	A (sec ⁻¹)	Correlation coefficient
1	42.049	1.2×10^{11}	0.988
2	86.966	6.5×10^{25}	0.988
3	19.405	3.3×10^3	0.988
4	11.582	6.4	0.988
5	7.901	<1	0.988
6	46.036	1.6×10^{12}	0.994
7	47.473	3.6×10^{12}	0.995
8	50.517	1.3×10^{14}	0.998
9	32.679	1.4×10^8	0.998
10	23.706	1.2×10^5	0.998
11	14.584	8.6×10^1	0.998
12	9.765	<1	0.998
13	91.972	1.9×10^{27}	0.992
14	93.897	2.0×10^{27}	0.993
15	97.782	4.6×10^{28}	0.995
16	60.987	6.7×10^{17}	0.999
17	55.505	3.8×10^{15}	0.999

TABLE 14

RESULTS FROM SATAVA'S METHOD FOR TRACE 2

Function No.	E (kcal mol ⁻¹)	A (sec ⁻¹)	Correlation coefficient
1	44.172	7.0×10^{11}	0.989
2	91.183	2.0×10^{27}	0.989
3	20.496	8.2×10^3	0.989
4	12.362	1.3×10^1	0.989
5	7.865	<1	0.989
6	47.887	7.6×10^{12}	0.994
7	49.217	1.5×10^{13}	0.995
8	52.021	4.5×10^{14}	0.997
9	33.691	3.2×10^8	0.997
10	24.475	2.4×10^5	0.997
11	15.121	2.4×10^2	0.997
12	10.214	2.4	0.997
13	95.872	4.4×10^{28}	0.992
14	97.655	4.2×10^{28}	0.993
15	101.250	> 10^{30}	0.995
16	61.250	1.1×10^{18}	0.999
17	56.582	9.5×10^{15}	0.999

obtained by other methods. Kinetic parameters obtained by using the present method for two runs agree with each other excellently. It is, therefore, concluded that the thermal dehydroxylation of $\text{Mg}(\text{OH})_2$ in our thermogravimetric traces follows the n type of mechanism with $n = 1.6$, activation energy of $53.2 \text{ kcal mol}^{-1}$ and frequency factor of $1.4 \times 10^{15} \text{ sec}^{-1}$. Thermal dehydroxylation of $\text{Mg}(\text{OH})_2$ has been investigated by many authors both isothermally and dynamically. A review has been written by Sharp⁹. The activation energy obtained by different authors varies considerably. The value obtained in the present case agrees with that reported in our previous paper¹⁰.

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