KINETICS OF THE THERMAL DECOMPOSITION OF CADMIUM CARBONATE (CdCO$_3$)

G. Bultosa* and A. M. Mulokozi**

*Alemaya University of Agriculture, P.O.Box 138, Dire Dawa, Ethiopia
**Department of Chemistry, University of Dar-es-Salaam, P.O.Box 35061, Dar-es-Salaam, Tanzania

Abstract

Cadmium carbonate used in the study was prepared from cadmium chloride, ammonium carbonate and ammonia. The X-ray powder diffraction, infrared spectral and chemical analysis conducted on the product show that the sample is of analytically acceptable purity. The thermal decomposition kinetics of cadmium carbonate was then studied by using the isothermal thermogravimetric method under a flow of dry nitrogen gas. The decomposition kinetics is best described by a two-dimensional phase boundary reaction mechanism (R_2). An activation energy (E_a) of 135.006 kJ·mol^{-1} and natural logarithm of the frequency factor (ln$Z$) of 16.754 were obtained in the range of 9 temperatures (400, 390, 380, 370, 360, 350, 340, 330 and 320°C).

Keywords: cadmium carbonate, kinetics

Introduction

While extensive work has been carried out on the decomposition kinetics of alkaline earth carbonates [1–11], few papers have been published on the decomposition kinetics of heavy metal carbonates [12–14]. In this paper, the kinetics of the thermal decomposition reaction of cadmium carbonate (1) under isothermal condition is reported.

$$CdCO_3 \text{ (s)} \rightarrow CdO \text{ (s)} + CO_2 \qquad (1)$$
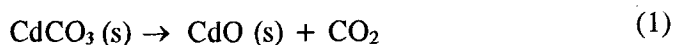
The kinetics of many solid-state reaction of the above type can be described by:

$$g(\alpha) = kt \qquad (2)$$

Where; $g(\alpha)$ represents one of the various reaction models applicable to solid-state decomposition reactions, α is the degree of decomposition, k the decomposition rate constant, and t the time. Under isothermal conditions the rate constant at any fixed temperature is usually determined from a plot of $g(\alpha)$ *vs.*
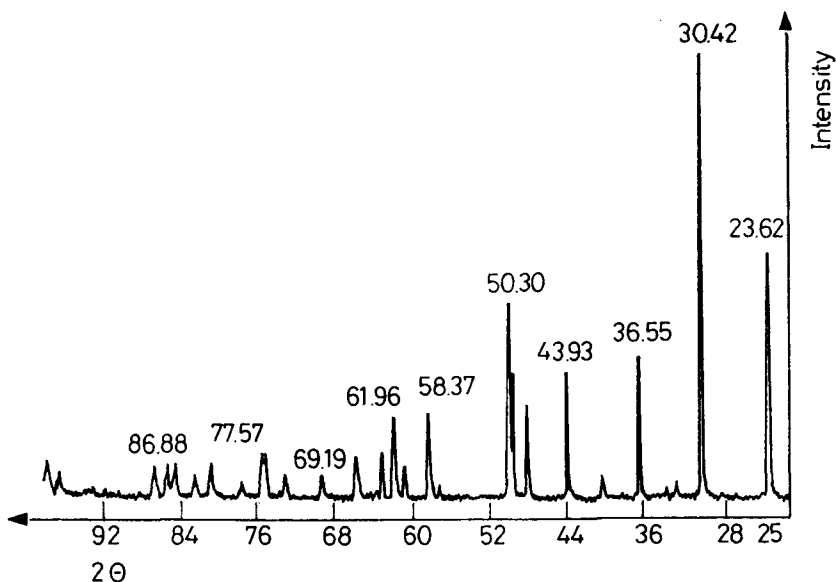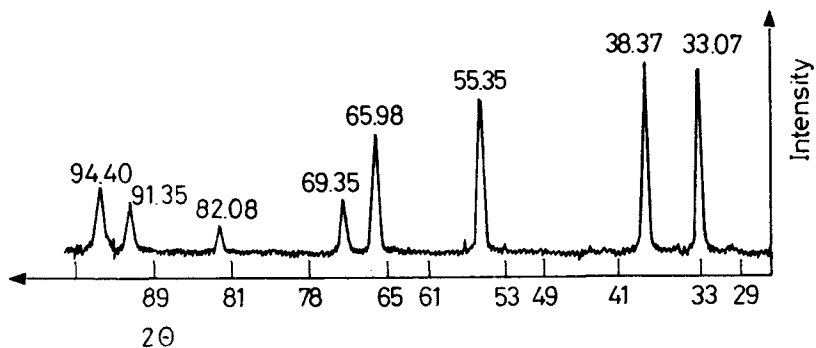
Fig. 1 Diffractogram of cadmium carbonate

Fig. 2 Diffractogram of cadmium oxide

time provided that the kinetic data from the thermoanalytical curves give a rectilinear Arrhenius plot for the selected mechanism. From the slopes of the $g(\alpha)$ vs. time plots, a series of k values are obtained. These are used to construct the Arrhenius plot of $\ln k$ vs. $1/T$. The slope of the Arrhenius plot gives the activation energy as $-E_a/R$, and the frequency factor as the intercept.

Experimental

The cadmium carbonate used in the studies was prepared from cadmium chloride supplied by MAY and BAKER LTD., England, ammonium carbonate
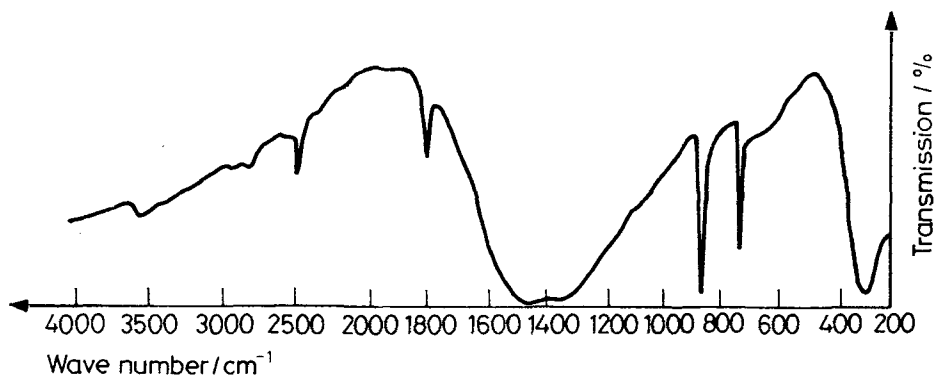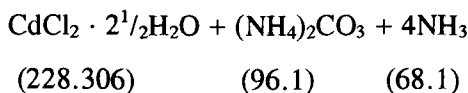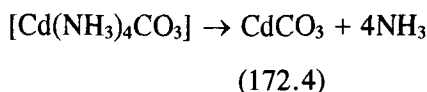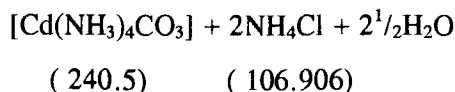
Fig. 3 Infrared spectrum of cadmium carbonate

and ammonia solution supplied by RIEDL-DEHAEN, Germany, according to the procedure in [15]. The chemical equations are:

$$CdCl_2 \cdot 2^1/_2H_2O + (NH_4)_2CO_3 + 4NH_3$$

$$(228.306) \qquad (96.1) \qquad (68.1)$$

$$\downarrow$$

$$[Cd(NH_3)_4CO_3] + 2NH_4Cl + 2^1/_2H_2O$$

$$(240.5) \qquad (106.906)$$

$$[Cd(NH_3)_4CO_3] \rightarrow CdCO_3 + 4NH_3$$

$$(172.4)$$

The resulting white crystals were filtered through sintered glass crucibles of porosity No. 3. The yield was 67%.

Since the presence of impurities generally affects the kinetic parameters [16], classical chemical analysis, X-ray powder diffraction and infrared spectral studies were conducted in order to confirm the purity. The X-ray diffraction pattern was taken with a compact X-ray diffraction analyzer operated at 40 KV/55MA employing CuK_α radiation and a nickel filter. The diffractograms for $CdCO_3$ and the corresponding oxide (CdO) are given in Figs 1 and 2 from which the diffraction pattern data were calculated (Tables 1 and 2). The interplanar distance calculated using the Braggs equation were in agreement with the standard diffraction pattern [17, 18].

The sample used for infrared spectral studies was prepared by using the potassium bromide (KBr) pellet technique, and the spectrum (Fig. 3) was taken in the range of 4000 to 200 cm^{-1}. The infrared active vibrations V_2, V_3 and V_4

Table 1 The diffractogram data for cadmium carbonate

Calculated			Standard		
2θ	θ	d/n	2θ	θ	d/n
23.620	11.810	3.767	23.52–23.54	11.76–11.77	3.780
30.420	15.210	2.938	30.28–30.30	15.14–15.15	2.950
33.060	16.530	2.710	32.92–32.94	16.46–16.45	2.720
36.550	18.275	2.458	36.52–36.54	18.26–18.27	2.460
40.260	20.130	2.240	40.16–40.18	20.08–20.09	2.245
43.930	21.965	2.061	43.82	21.91	2.066
48.220	24.110	1.887	48.14–48.16	24.07–24.8	1.890
49.630	24.815	1.837	49.58–49.60	24.79–24.8	1.838
50.300	25.150	1.814	49.96–49.98	24.98–24.99	1.825
58.370	29.185	1.581	58.32–58.34	29.16–29.17	1.582
60.880	30.440	1.522	60.86–60.88	30.43–30.44	1.522
61.960	30.980	1.498	61.84–61.86	30.92–30.93	1.500
63.130	31.565	1.473	63.10–63.12	31.55–31.56	1.473
65.710	32.855	1.421	65.60–65.62	32.80–32.81	1.423
69.190	34.595	1.358	69.22–69.24	34.61–34.62	1.357
73.100	36.550	1.295	73.20	36.6	1.293
75.190	37.595	1.264	75.22–75.24	37.61–37.62	1.263
75.410	37.705	1.261	75.44–75.46	37.72–37.73	1.260
77.570	38.785	1.231	77.46–77.48	38.73–38.74	1.232
80.840	40.420	1.189	80.84	40.42	1.189
82.360	41.180	1.171	82.42–82.44	41.21–41.22	1.171
84.560	42.280	1.146	84.54–84.56	42.27–42.28	1.146
85.500	42.750	1.136	85.38	42.69	1.137
86.880	43.440	1.121	86.90	43.45	1.121
93.660	46.830	1.057	93.66	46.83	1.057
96.720	48.360	1.032	96.66	48.33	1.032
97.870	48.935	1.022	97.78–97.80	48.89–48.9	1.023

(Fig. 4) are typical for carbonate [19, 20]. The absorption frequencies are summarized in Table 3. The normal mode of vibration V_4 observed at 736 cm^{-1} compares with that for calcite at 706 cm^{-1}. The difference is attributed to the influence of the metal cation.

The results of X-ray powder diffraction, infrared spectral and chemical analysis (Table 4) and direct mass calculations from the thermoanalytical curve (Fig. 5) all support that the prepared product is of analytically acceptable purity. A kinetic study of the thermal decomposition reaction was then conducted on this sample.
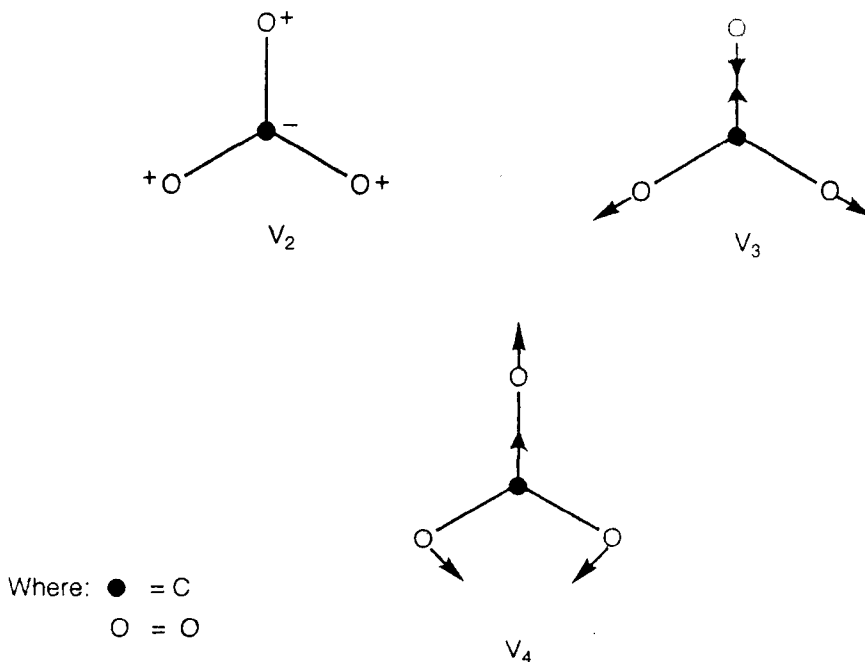
Fig. 4 Normal modes of vibration of planar XY_3 molecules (where X: is divalent metal cation and Y_3 is carbonate)

Table 2 The diffractogram data for cadmium oxide

Calculated			Standard		
2θ	θ	d/n	2θ	θ	d/n
33.070	16.535	2.709	33.04–33.06	16.52–16.53	2.710
38.370	19.185	2.346	38.30–38.32	19.15–19.16	2.350
55.350	27.675	1.660	55.34–55.36	27.67–27.68	1.660
65.980	32.990	1.416	65.96–65.98	32.98–32.99	1.416
69.350	34.675	1.355	69.34–69.36	34.67–34.68	1.355
82.080	41.040	1.174	82.06–82.08	41.03–41.04	1.174
91.350	45.675	1.078	91.40	45.7	1.077
94.400	47.240	1.050	94.48–94.50	47.24–47.25	1.049

Kinetic studies

Thermogravimetric studies were carried out in a flow of dry nitrogen gas (10.5 ml/min) with a Mettler TG 50 thermobalance with a TC 10A processor and an Epson Fx-800 recorder system. The sample mass was between 35.4 and 36.4 mg for all runs in order to maintain the same effect of the sample mass on

Table 3 The vibrational frequencies (cm^{-1})

Cadmium carbonate	Calcite (CaCO₃)	MgCO₃	Type of normal mode vibration
736	706	735	V_4
870	879	-	V_2
1360–1460	1429–1492	1460	V_3
1796			
2490			
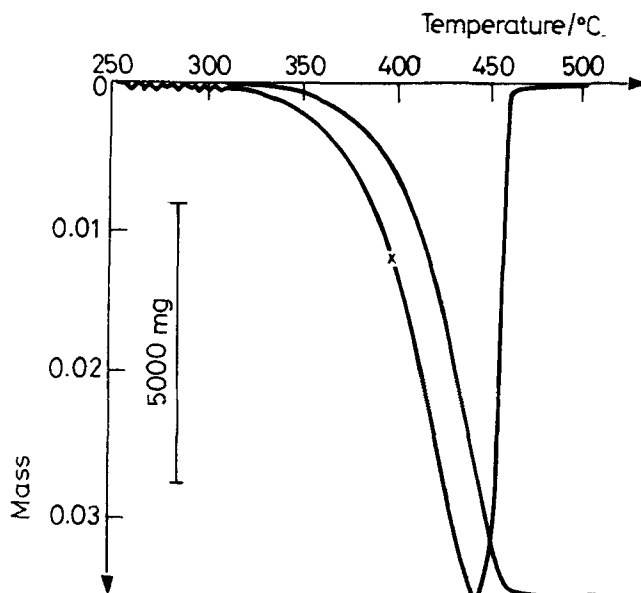
Fig. 5 The nonisothermal TG curve at heating rate of 10 deg·min⁻¹ for the decomposition of cadmium carbonate

the kinetic parameters. A platinum crucible of maximum capacity of 600 mg was used in all runs.

Results and discussion

The decomposition of cadmium carbonate starts at around 280°C and ends at around 500°C (Fig. 5). The isothermal study was therefore undertaken in the temperature range from 320 to 400°C. A representative isothermal thermoanalytical curve is shown in Fig. 6. The plots of α vs. time, min, (Fig. 7) are typical of solid-state decomposition reactions. The moving phase boundary mechanism model which normally applies to the decomposition of divalent met-

Table 4 The summary of chemical analysis result

	Cd^{2+}	CO_3^{2-}	CO_2
		%	
Classsical chemical analysis	65.414	35.051	25.704
Direct calculation from the TG curve	65.205	34.789	25.512
Theoretical	65.197	34.802	25.522
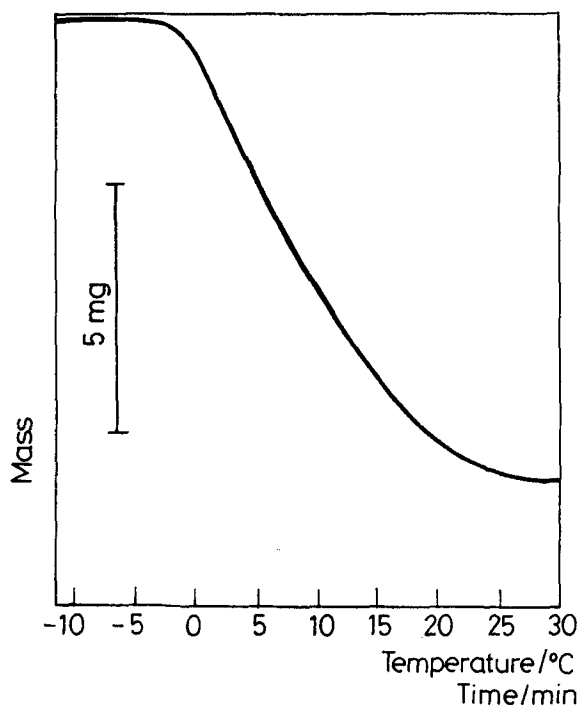
Fig. 6 The isothermal TG curve at 400 °C, $m=35.487$ mg for the decomposition of cadmium carbonate

al carbonates was used to analyze the kinetic data [1–11]. Accordingly, the measured kinetic data are compatible with the R_2 mechanism (3).

$$kt = 1- (1 - \alpha)^{1/2} \ (R_2) \qquad (3)$$

The rate constants determined from the slope of the t(min) vs. $1-(1-\alpha)^{1/2}$ plot (Fig. 8) are summarized in Table 5. Based on the data, the plot of $\ln k$ vs.
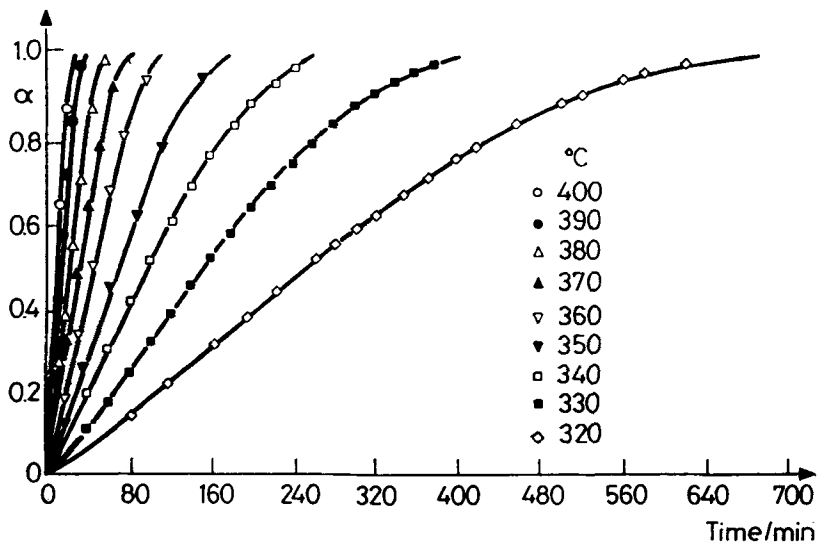
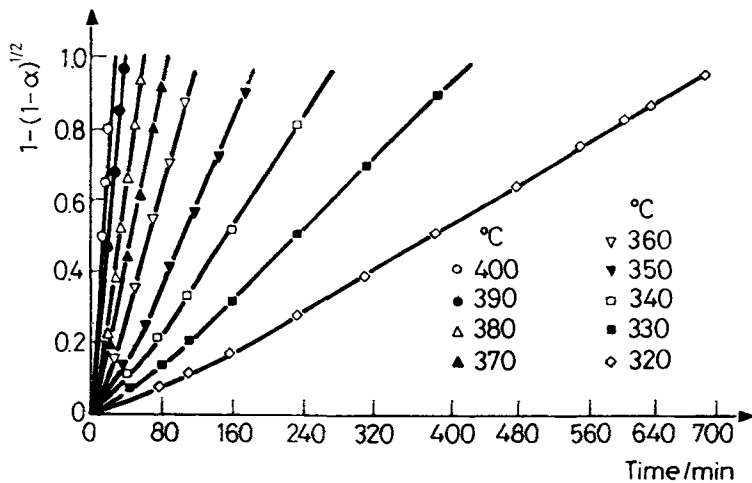**Fig. 7** A plot of α vs. t, min for nine isothermal temperatures

Fig. 8 Plot of t, min vs. $1-(1-\alpha)^3$

$1/T$ (Fig. 9) gave $-E_a/R$, and from this the activation energy $E_a = 135.006$ kJ·mol^{-1} was obtained. The intercept gave $\ln Z = 16.754$. The value of the activation energy obtained compares with the lowest reported value, $E_a = 147$ kJ·mol^{-1} for calcite [10]. In both compounds the decomposing group is CO_3^{2-} and the rate-determining step is probably the breaking of the C–O bond. The discrepancy may be related to the influence of the experimental conditions
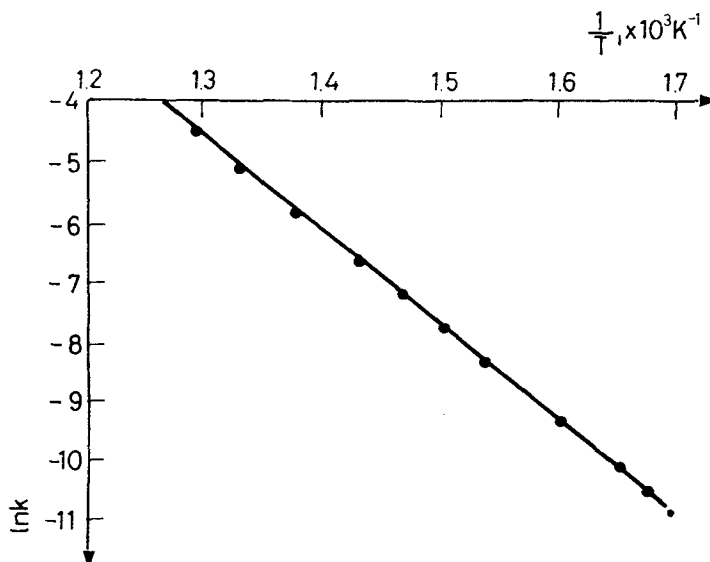
$$\frac{1}{T}, \times 10^3 \mathrm{K}^{-1}$$

Fig. 9 The Arrhenius diagram

Table 5 The value of ln$k$ vs. isothermal temperature

T / °C	$1/T \times 10^3$ K	k	$-\ln k$
320	1.68591	2.372×10^{-5}	10.6491
330	1.65796	3.943×10^{-5}	10.1409
340	1.63092	6.015×10^{-5}	9.7186
350	1.60475	9.041×10^{-5}	9.3111
360	1.57940	1.419×10^{-4}	8.8603
370	1.55484	1.996×10^{-4}	8.5191
380	1.53104	2.933×10^{-4}	8.1343
390	1.50795	4.536×10^{-4}	7.6982
400	1.48555	6.246×10^{-4}	7.3283

$E = 135.006$ kJ mol^{-1}; ln$Z = 16.754$; $r = 0.999$

and the metal cation. The Cd–O bond is more covalent than the Ca–O bond [21], which tends to weaken the C–O bond, and hence reduces the value of activation energy of the decomposition of CdCO$_3$.

Conclusions

Since small sample masses were used, the problem of heat transfer was reduced to a minimum. The use of CdCO$_3$ powder also ensures the rapid diffusion

of CO_2 and minimizes the effect of mass transport. Under these experimental conditions, the value of the activation energy obtained can be regarded reliable.

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Zusammenfassung — Das in der Untersuchung verwendete Kadmiumkarbonat wurde aus Kadmiumchlorid, Ammoniumkarbonat und Ammoniak hergestellt. Am Produkt durchgeführte Pulver-Röntgendiffraktion, Infrarotspektral- und chemische Analyse zeigen, daß die Probe von analytisch annehmbarer Reinheit ist. Mittels isothermer gravimetrischer Methode unter trockenem Stickstoffgasfluß wurde dann anschließend die Kinetik der thermischen Zersetzung von Kadmiumkarbonat untersucht. Die Zersetzungskinetik wird am besten durch eine zweidimensionalen Phasengrenzschicht-Reaktionsmechanismus (R_2) beschrieben. Im Bereich von 9 Temperaturen (400, 390, 380, 370, 360, 350, 340, 330 und 320°C) wurde eine Aktivierungsenergie von $E_a = 135.006$ kJ/mol und für den Frequenzfaktor ein natürlicher Logarithmus (lnZ) von 16.754 gefunden.