KINETIC STUDY OF THE THERMAL DECOMPOSITION
# OF COBALT(III) OXYHYDROXIDE
I. Isothermal kinetic data

L. Hernan, J. Morales, A. Ortega* and J. L. Tirado

DEPARTAMENTO DE QUÍMICA INORGÁNICA, FACULTAD DE CIENCIAS,
UNIVERSIDAD DE CÓRDOBA, SPAIN

The kinetics of thermal decomposition of CoOOH have been studied by analysis of iso-
thermal weight loss data under vacuum. The comparison of linear correlation coefficients
of different kinetic expressions applied to these data does not allow an understanding of
the mechanism, even when significance tests are performed (t test). A single value of the
activation energy (193 kJ mol^{-1}) is obtained from the Arrhenius plots, and is relatively
independent of the choice of rate law. On the other hand, a change in the mechanism of
formation of Co_3O_4 with temperature cannot be inferred from analysis of isothermal
data. Thus, the statement of some authors that from formal kinetics it is possible to dis-
tinguish the proton and electron transfers involved in the transformation appears unac-
ceptable.

A few years ago, Avramov [1, 2] stated that it is possible to distinguish the two
physico-chemical processes involved in the thermal decomposition of CoOOH from
kinetic analysis of the isothermal weight loss data. The first process is a proton transfer
between two hydroxyl groups, and the second is an electron transfer from an oxide
ion to a Co(III) ion. The resulting reaction is endothermic in nature, and has the
stoichiometry:

$$12\ CoOOH \rightarrow 4\ Co_3O_4 + 6\ H_2O + O_2 \tag{1}$$
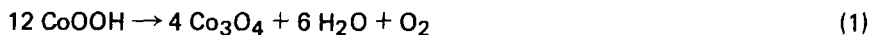
in which oxygen and water are released simultaneously. According to Avramov, the
contracting area rate law proved applicable and two values of activation energy were
reported 145 and 79 kJ mol^{-1}, below and above 280°, respectively.

However, the experimental conditions used in his study (static air atmosphere and
a large amount of sample: 1g) are not the most appropriate for this reaction, which
involves gaseous products. Special control is necessary to prevent the development of
a gas layer around the solid. In this way, the effect of the partial pressure of the
evolved gas on the equilibrium decomposition temperature and the problems related
to its diffusion should be minimized.

* Present address: Departamento de Química Inorgánica, Facultad de Química, Universidad de
Sevilla, Spain.

6*

Another difficulty concerns the self-cooling effect of an endothermic reaction, pointed out by Gallagher et al. [3]. This effect can play an important role, since differences in temperature between the sample and its container become possible. As the sample weight is increased, high temperature gradients develop and hence the heat transfer process can be a major factor in the control of the reaction.

O'Brien et al. [4] have recently studied the kinetics of reaction (1), under a nitrogen flow. Above 300°, the process appears to follow a mechanism controlled by the phase boundary in two dimensions, with an activation energy of 101 kJ mol^{-1}. Below 290°, a mechanism which follows an Avrami–Erofeev equation operates, the activation energy being 214 kJ mol^{-1}. However, it is worth noting that these authors used a wide range of temperatures, from 290 up to 391°. In our opinion, the temperatures in the upper portion of this range are too high, leading to serious inconveniences, among them the short time required for completion of the reaction (13 minutes for the run at 301°, 2 minutes at 341°). Deviations from true isothermal conditions, extending over a wide range of degree of conversion, probably occur, and the temperature inhomogeneities will affect the accuracy of the reaction rate measurements. These factors cannot be neglected in the reliability of the conclusions obtained by O'Brien in the kinetic analysis of CoOOH decomposition.

From the above observations, additional results are necessary to elucidate, if possible, the kinetics of reaction (1), precautions being taken to remove the product gases and reach a reasonable time for high degrees of conversion. The results reported relate to this aim. A detailed study of non-isothermal data will appear in part II, in which textural, morphological and structural information will provide a better understanding of the thermogravimetric results.

Experimental

Material

A polycrystalline sample of CoOOH was synthetized according to the method in [5]. The powder was introduced into a Phaxe 2005 pressure vessel for 11 days at 120° to improve the crystallinity. X-ray diffraction patterns of the product dried for several hours at 100° show reflections that can be assigned to CoOOH exclusively. Electron micrographs of this sample revealed plate-shaped particles with well-defined contour lines. The mean particle diameter was about 0.1 μm. Besides these particles, a more finely divided powder could be observed, probably due to non-uniform crystal growth in the pressure vessel.

Methods

The isothermal weight loss was recorded with a model RG Cahn electrobalance connected to a vacuum line (10^{-4} Torr). After evacuation, the sample was inserted into a furnace preheated to the desired temperature. After an interval of several

minutes for thermal equilibrium to be reached, data collection was started. Temperatures were measured with a chromel—alumel thermocouple and recorded on a Yokawa apparatus. The error in temperature was estimated as ±1 degree.

Nine kinetic expressions were applied to the data; these represent three sets of reactions: (i) reactions which follow an Avrami—Erofeev equation, (ii) phase boundary-controlled and first-order reactions, and (iii) diffusion-controlled reactions. Table 1 includes the functions that were plotted against time. With the use of the least squares method, the slopes m of the plots (associated with the rate constant of the process) and the correlation coefficients r were calculated.

Two main statistical criteria can be used to compare correlation coefficients at a chosen level of significance. When the F-test criterium is used [6] to differentiate which of two kinetic expressions (labelled 1 and 2) is the more accurately fulfilled, the critical ratio can be obtained from $r_{t,1}$ and $r_{t,2}$. However, it must be assumed that there is not a linear dependence between the two sets of data corresponding to 1 and 2; in other words, the value of $r_{1,2}$ must be low. Since the functions in Table 1 display a reasonable correlation [7] over the α range 0.05–0.90, it is necessary to show caution in interpreting the critical values obtained.

On the other hand, the use of a critical ratio t, defined as:

$$t = \frac{|r_{t,2} - r_{t,1}| \sqrt{(N-3)(1+r_{2,3})}}{\sqrt{2(1 - r_{1,2}^2 - r_{t,1}^2 - r_{t,2}^2 - 2r_{1,2}r_{t,1}r_{t,2})}} \tag{2}$$

where N is the number of measured points, may provide a better parameter in order to contrast a hypothesis about the meaning of the differences between $r_{t,1}$ and $r_{t,2}$ when the sets of data 1 and 2 are related. If this ratio is larger than the appropriate critical value at the chosen significance level and degrees of freedom, it can be admitted that the kinetic law of higher r describes the reaction more accurately.

Table 1 Algebraic functions, $g(\alpha)$, used in the analysis

	Mechanism	$g(\alpha)$
F_1	First-order	$-\ln(1-\alpha)$
R_2	Contracting area	$1-(1-\alpha)^{1/2}$
R_3	Contracting volume	$1-(1-\alpha)^{1/3}$
A_2	Avrami—Erofeev	$[-\ln(1-\alpha)]^{1/2}$
A_3	Avrami—Erofeev	$[-\ln(1-\alpha)]^{1/3}$
D_1	One-dimensional diffusion	α^2
D_2	Two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3	Three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$
D_4	Ginstling—Brounshtein	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

Results and discussion

Figure 1 shows the isothermal (α, t) measurements recorded in the temperature range 236—268°. It can be observed that the reaction develops slowly and the magnitude of α reaches an asymptotic value with time at the lowest temperature. Above 268° the time required to attain isothermal conditions can be compared with
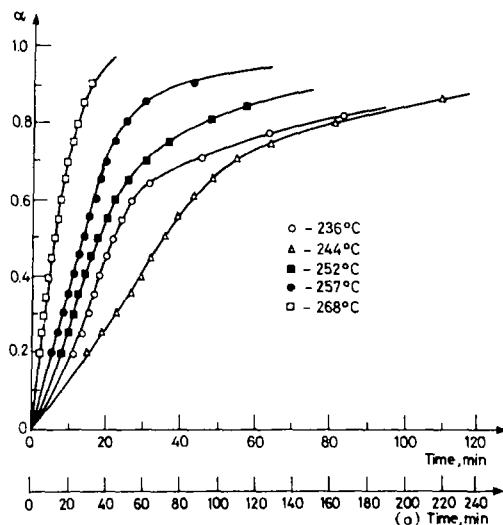

Fig. 1 Isothermal (α, t) measurements in the temperature range 236—268°C

that used for completion of the reaction, and experimental errors can affect the conclusions obtained from the kinetic analysis at this temperature.

The rate constants and linear regression coefficients of the plots of the functions in Table 1 versus time are listed in Table 2. Typical plots are shown in Fig. 2. In the low-temperature region, a clear deviation from linearity is observed for any kinetic law employed in the analysis. The graph (Fig. 2a) shows a change in slope, located at $\alpha \sim 0.6$, which corresponds to the (α, t) point that starts the desacceleratory stage in a more accentuated way. With increasing temperature, reasonably straight lines are obtained for all kinetic expressions (Fig. 2b).

The values of the critical ratio t obtained in the comparison of the correlation coefficients of the 9 selected rate expressions are included in Table 3. The interdependence of the $g(\alpha)$ functions was evident in the r values $(r_{1,2})$, which were always higher than 0.95. At the lowest temperature (236°), the diffusion model D_3 gives significant critical ratios when compared with the remaining kinetic expressions, this being a direct indication that this model is statistically more acceptable. With increasing temperature, it is not possible to find a mechanism that excludes the others significantly. Nevertheless, a diffusion model seems to be inadequate at higher temperatures, as shown by the t parameter (see Table 3). A conclusion emerges from a

Table 2 Slopes (m) and linear correlation coefficients (r) of $g(\alpha)$ vs time plots. (α range 0.20–0.9; at 509 K: 0.2–0.8)

Temperature, °C	236		244		252		257		268	
Mechanism	r	$m \cdot 10^3$	r	$m \cdot 10^2$	r	$m \cdot 10^2$	r	$m \cdot 10^2$	r	$m \cdot 10^2$
F_1	0.9359	9.41	0.979	1.912	0.9768	3.18	0.9974	7.13	0.9938	14.08
A_2	0.8881	5.12	0.951	1.005	0.9449	1.69	0.9858	3.56	0.9982	7.16
A_3	0.8687	3.55	0.937	0.690	0.9302	1.16	0.9767	2.41	0.9944	4.87
R_2	0.8995	2.96	0.954	0.578	0.9507	0.97	0.9849	2.03	0.9975	4.07
R_3	0.9123	2.30	0.963	0.453	0.9603	0.76	0.9911	1.62	0.9985	3.23
D_1	0.9209	4.18	0.961	0.809	0.9617	1.37	0.9845	2.82	0.9950	5.65
D_2	0.9464	3.22	0.977	0.643	0.9788	1.08	0.9928	2.33	0.9916	4.61
D_3	0.9708	1.18	0.990	0.249	0.9922	0.41	0.9899	0.96	0.9731	1.88
D_4	0.9557	8.48	0.983	0.172	0.9844	0.28	0.9937	0.63	0.9871	1.25

Table 3 Values of the critical ratio t obtained by comparing the linear correlation coefficients of the nine kinetic expressions. The selected significance level was 99.95%

236°C

	A_2	A_3	R_2	R_3	D_1	D_2	D_3	D_4	
	6.82	6.77	10.17	10.25	4.68	2.18	5.68	3.71	F_1
D_4	—	6.26	2.65	4.55	2.91	4.65	6.54	5.33	A_2
D_3	2.47	—	4.08	5.14	3.54	4.97	6.73	5.96	A_3
D_2	3.45	2.86	—	9.71	3.00	5.21	7.44	5.44	R_2
D_1	3.96	3.62	4.00	—	1.53	4.55	6.76	9.04	R_3
R_3	2.60	2.95	2.14	0.81	—	8.76	9.25	9.05	D_1
R_2	3.12	3.41	2.80	1.24	6.13	—	8.91	9.29	D_2
A_3	3.36	3.85	3.02	2.04	3.76	2.84	—	8.92	D_3
A_2	2.90	3.36	2.54	1.20	3.02	1.05	5.13	--	D_4
F_1	0.89	1.83	0.77	20.04	5.72	5.77	4.86	4.56	
	D_4	D_3	D_2	D_1	R_3	R_2	A_3	A_2	

244°C

252°C

	A_2	A_3	R_2	R_3	D_1	D_2	D_3	D_4	
	6.47	6.70	9.11	8.97	13.45	0.69	3.57	2.22	F_1
D_4	—	6.56	2.01	4.18	2.17	3.82	5.32	4.39	A_2
D_3	3.74	—	3.84	5.00	3.01	4.33	5.87	4.87	A_3
D_2	4.93	6.45	—	8.89	2.20	4.15	5.44	4.69	R_2
D_1	4.31	0.58	2.50	—	0.37	3.41	4.89	4.08	R_3
R_3	3.26	2.49	3.84	5.77	—	6.05	5.94	6.10	D_1
R_2	5.94	0.30	1.20	0.41	5.41	—	5.04	5.67	D_2
A_3	11.7	1.33	2.26	1.61	0.51	2.35	—	4.56	D_3
A_2	2.94	0.71	2.08	0.79	0.22	0.76	0.64	—	D_4
F_1	4.09	1.45	2.44	1.60	0.65	1.89	0.60	1.28	
	D_4	D_3	D_2	D_1	R_3	R_2	A_3	A_2	

257°C

* Run at 236°C, critical t value: 4.59. Runs at 244 and 252°C, critical value: 4.44. Run at 257°C, critical value: 4.32.

comparison of the results in Tables 2 and 3: the conventional procedures of plotting the values of $g(\alpha)$ versus time are not able to provide an accurate understanding of the reaction mechanism that controls the thermal decomposition of CoOOH over the considered temperature range. This result contrasts with those obtained by Avramov [2] and O'Brien [4], who firmly state the mechanism of reaction (1) from the analysis
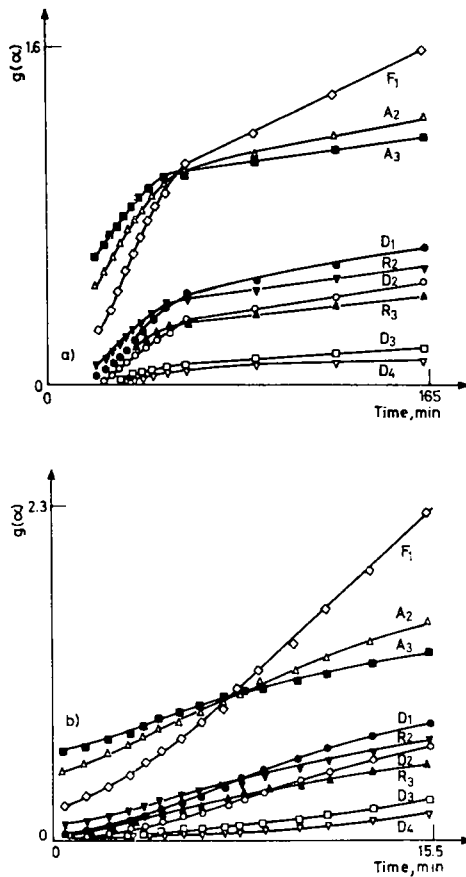
Fig. 2 Plots of $g(\alpha)$ vs time for two representative temperatures: a) 236°C, b) 268°C

of a particular function in Table 1 against time. However, in their papers no statistical methods were employed to determine the level of accuracy to which a certain kinetic expression is fulfilled preferentially. Moreover, the different conclusions reported by those authors are consistent with the results in Tables 2 and 3, since a reliable distinction between the kinetic models is not found.

The Arrhenius plots for F_1, R_2, A_2 and D_3 kinetic laws, taken as representative examples of each group of reaction mechanisms, are shown in Fig. 3. The activation energy values obtained from the slopes of these plots are relatively independent of the choice of the rate law. Such behaviour has also been found in different kinetic studies of solid-state reactions [8, 9]. Criado et al. [7] have recently proposed a theoretical explanation on the basis of the correlations shown within the $g(\alpha)$ functions for a wide range of decomposed fraction, α.

As the deviations in the slopes of the Arrhenius plots for any kinetic law are small, a single average activation energy value, 193 kJ mol^{-1}, with standard deviation

± 4 kJ mol^{-1}, has been computed for the process. This result also differs from those in previous investigations [1, 2], in which two activation energy values were reported. However, serious uncertainties arise from the results of Avramov [2], since the difference in the activation energy is evaluated from a graph in which only 6 points were plotted. If a least squares procedure is applied to these data, acceptable linearity is obtained (regression coefficient 0.989) and a single activation energy of 109 kJ mol^{-1} can be calculated.
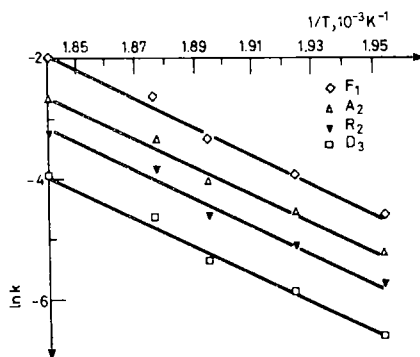
Fig. 3 Arrhenius plots of four selected kinetic laws

A clearer change in the slope of the Arrhenius plot is shown by the data obtained by O'Brien et al. [4]. However, the less steep line starts at 314°, a temperature at which 90% conversion is reached in a period of approximately 2 minutes. Under these conditions deviation from the true isothermal state may occur during the course of the reaction and the errors in rate measurement would be sufficiently large not to be neglected. Nevertheless, the activation energy found in the lower temperature region, 209 kJ mol^{-1}, is slightly higher than that obtained in this paper, the difference probably being due to the use of N_2 atmosphere.

A way that may overcome the difficulty of discerning the kinetic law that accurately describes a solid-state reaction has been pointed out by several authors [10, 11] in the use of a reduced time plot, that can be compared with the graphs obtained for the theoretical equations.

Figure 4 shows such a plot for our data. Some of the functions of Table 1 have been included for comparison. It can be observed that the values of α do not seem to obey any of the kinetic laws in Table 1 and the distinction of the operating kinetics becomes uncertain for reaction (1). We would also like to draw attention to the procedure used by some authors [12] to differentiate various stages in the reduced time plots, each one being analyzed by a certain kinetic law. Besides the inherent errors in the decision of the limits where a particular mechanism operates, misleading results may occur, since the values of rate constants may diminish with increasing temperature [12].

The method of comparison of the kinetics of an isothermal solid-state reaction based on the slope, m, of the plot $\ln \left[-\ln (1 - \alpha) \right]$ vs $\ln t$ (see Table 1) has also been
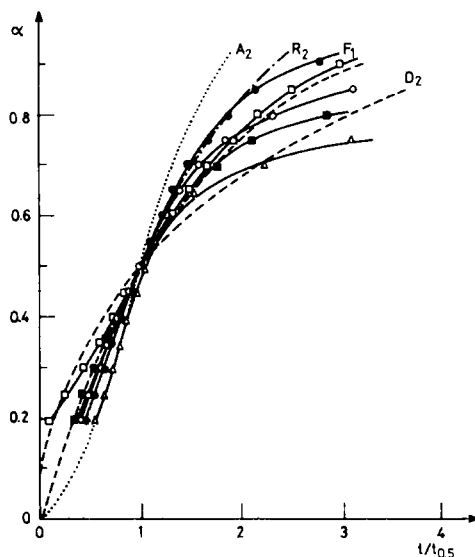
Fig. 4 Reduced time plots of some of the kinetic functions in Table 1 and the isothermal data at different temperatures

applied to our data. Some typical plots in the interval $0.2 \leqslant \alpha \leqslant 0.65$ are shown in Fig. 5. A clear deviation from linearity is observed for the isothermal run at 268°, especially at low degrees of conversion. This fact is probably due to a departure from true isothermal conditions at this stage of the reaction and substantiates the advantage of working at lower temperatures and smaller reaction rates. The linear regression coefficients and the slopes of the plots in Fig. 5 are given in Table 4. It may be observed, that the plots are not identical in shape, and the value of m decreases almost parallel to the increase in temperature. A progressive change in mechanism, as has been suggested when the shape of the plot changes gradually [9], seems doubtful for the decomposition of CoOOH, in light of the results discussed above.
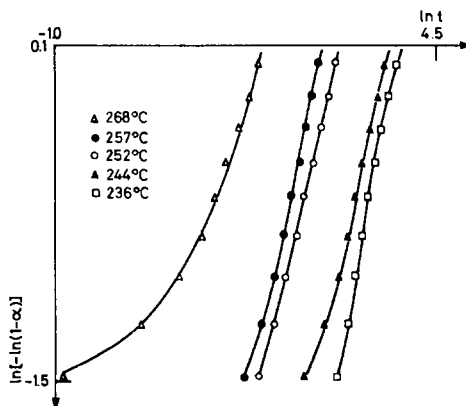

Fig. 5 Plots of $\ln [-\ln (1-\alpha)]$ vs $\ln t$

Table 4 Slopes (m) and linear correlation co-
efficients (r) of $\ln [- \ln (1 - \alpha)]$ vs
$\ln t$ plots (α) range 0.20—0.65

Temperature, °C	m	r
236	1.54	0.9906
244	1.26	0.9964
252	1.22	0.9990
257	1.22	0.9943
268 *	0.95	0.9980

* α range 0.35—0.65.

Summary and conclusions

The present study on the kinetics of thermal decomposition of CoOOH rules out a knowledge of the mechanism through analysis of isothermal weight loss data exclusively, in contrast to previous investigations on this subject.

A complex Arrhenius dependence on temperature is not observed, and the statement that from formal kinetics it is possible to differentiate the proton and electron transfers that simultaneously accompany the formation of the spinel Co_3O_4 is unfortunately too attractive to be true.

The only conclusion that seems acceptable in light of the above results is a single value (193 kJ mol^{-1}) for the activation energy. Such a value is relatively independent of the rate law used in the calculation, and higher than that found in the dehydroxylation of other trivalent metal oxyhydroxides (e.g. γ-FeOOH [13], α-FeOOH [14], a difference that might be related to the electron transfer in reaction (1).

References

1 L. K. Avramov, Thermochim. Acta, 10 (1974) 409.

2 L. K. Avramov, Thermochim. Acta, 32 (1979) 235.

3 P. K. Gallagher and D. W. Johnson, Jr., Thermochim. Acta, 6 (1973) 67.

4 P. O'Brien and U. Patel, J. Chem. Soc. Dalton Trans. (1982) 1407.

5 R. G. Delaplane, J. A. Ibers, J. R. Ferraro and J. J. Rush, J. Chem. Phys., 50 (1969) 1920.

6 M. E. Brown and A. K. Galwey, Thermochim. Acta, 29 (1979) 129.

7 J. M. Criado, M. González, A. Ortega and C. Real, to be published.

8 J. M. Criado and J. Morales, J. Thermal Anal., 10 (1976) 103.

9 J. D. Hancock and J. H. Sharp, J. Amer. Ceram. Soc., 55 (1972) 74.

10 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, J. Amer. Ceram. Soc., 49 (1966) 379.

11 B. Delmon, Introduction à la Cinetique Hétérogène, Technip, Paris, 1969.

12 J. M. Gonzalez-Calbet and M. A. Alario Franco, Thermochim. Acta, 58 (1982) 45.

13 R. Giovanoli and R. Brütsch, Thermochim. Acta, 13 (1975) 15.

14 J. Lima de Faria, Z. Krist., 119 (1963) 176.

Zusammenfassung — Die Kinetik der thermischen Zersetzung von CoOOH wurde durch Analyse von im Vakuum unter isothermen Bedingungen erhaltenen Gewichtsverlustkurven untersucht. Ein Vergleich der linearen Korrelationskoeffizienten von verschiedenen auf diese Kurven angewandten kinetischen Ausdrücken trägt nicht zum Verständnis des Mechanismus bei, auch nicht bei Ausführung von Signifikanztesten (t-Test). Aus den Arrhenius-Diagrammen wird stets der gleiche Wert für die Aktivierungsenergie (193 kJ · mol^{-1}) erhalten, der verhältnismäßig unabhängig von der Wahl des Geschwindigkeitsgesetztes ist. Andererseits kann eine Änderung des Mechanismus der Bildung von Co$_3$O$_4$ mit der Temperatur nicht durch Analyse der isothermen Daten agbeleitet werden. Die Feststellung einiger Autoren, daß es moglich sei, den Protonen- und Elektronenübergang bei Umwandlungen aus der formalen Kinetik zu erkennen, kann somit nicht akzeptiert werden.

Резюме — Кинетика реакции термического разложения CoOOH исследована на основе анализа данных по изотермической потери веса в вакууме. Сопоставление линейных коэффициентов корреляции различных кинетических уравнений, используемых для анализа этих данных, не позволило понять механизм разложения даже при проведении смысловых проверок (t апробирование). Единственное значение энергии активации (193 кдж/моль), полученное на основе арре

ниусовских графиков, было относительно независимым от выбора закона скорости. С другой стороны, изменение с температурой механизма образования Co$_3$O$_4$ не может быть установлено на основе анализа изотермических данных. Таким образом, заявление некоторых авторов о том, что исходя из формальной кинетики представляется возможным различать перенос протона и электрона в реакции превращения, становится несостоятельным.