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DEHYDROXYLATION KINETICS OF SOME PURE SMECTITES

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ABSTRACT

Thermogravimetric curves were recorded for six smectites; Manito (U.S.A.) and Sampor (U.S.S.R.) nontronites, and Polkville (U.S.A.), Askangel (U.S.S.R.), Jelsovy Potok (C.S.A.) and Bakony (Hungary) montmorillonites. Kinetic analysis of the dehydroxylation wave was performed by using the first order equations of Horowitz and Metzger (1963), Coats and Redfern (1964), Dave and Chopra (1966), as well as the method of Šatava and Škvara (1969). A unimolecular nucleation mechanism seems to prevail, according to the last method, independent of diffusional effects. Nontronite dehydroxylation is associated with a higher activation energy (E_a) and preexponential factor (A), in comparison to the dehydroxylation of montmorillonite (mean $E_a = 39.1$ and 21.8 kcal mol^{-1}, respectively). The compensation effect, correlating E_a and log A, was found to hold and a formula was established.

INTRODUCTION

Smectites, when subjected to heat treatment, release water held in various manners and through different temperature ranges. On dehydration, free and oriented water molecules come out from the interlamellar spaces and from the hydrated shells of the exchangeable cations at different temperatures related to the type of those cations. At relatively higher temperatures (400–700 °C), dehydroxylation takes place yielding two water molecules per unit cell and a condensed non-expandable structure. Nontronites dehydroxylate at relatively lower temperatures compared with montmorillonites [1,2].

Dehydroxylation of montmorillonite has been studied by DTA [3,4], IR spectroscopy, X-ray analysis [5,6] and thermogravimetry [7]. This process is concluded to be slightly influenced, in addition to many other factors, by the interlayer cations [2]. Thermal methods of analysis (DTA and TG) have become recently increasingly important as valuable tools in the identification of clay minerals [8–12].

The present study deals with the dehydroxylation kinetics of six pure smectites samples prepared from varying localities (U.S.A., U.S.S.R., C.S.S.R.

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and Hungary), two of them are nontronites and the others are montmorillonites (iron and aluminium-rich smectites). Kinetic analysis of the TG traces is performed in order to evaluate the reaction order, activation energy and the pre-exponential factor characterizing dehydroxylation. This study is carried out with the purpose of demonstrating the role played by deposit locality in determining dehydroxylation kinetics of smectites.

EXPERIMENTAL

Materials

The tested materials are five smectites from various localities. These are; Manito (U.S.A.), Sampor (U.S.S.R.), Polkville (U.S.A.), Askangel (U.S.S.R.) and Jelsovy Potok (C.Š.A.). The first two samples are nontronites and the others are typical montmorillonites.

Purified samples were obtained from the above mentioned natural deposits by a method described earlier [13].

Chemical analysis of the purified smectites was carried out by conventional silicate analysis. The structural formulae are calculated and are given elsewhere [13].

Thermogravimetry

Thermal weight loss curves were recorded for the five smectites by an automatic thermobalance produced by Gebrüder Netzsch, West Germany, at a heating rate of 10 K $\min^{-1}$. In addition, the TG curve of montmorillonite from Bakony (Hungary), published by Liptay [14], was employed in the next kinetic analysis. This material was described as a characteristic montmorillonite free from any impurities detected by X-ray diffractometry. The curve recorded at a heating rate of 10 K $\min^{-1}$ was selected as comparable to the present recordings of the other smectites.

RESULTS

Weight loss associated with dehydroxylation

The recorded thermograms are graphically plotted in a previous paper [15]. The TG curves are segmented into two parts; the first covering the temperature range up to 350 °C (dehydration region) and the second covering the range beyond 350 °C (dehydroxylation region). The dehydration process has been discussed early in a previous work [15].

TABLE 1

Weight loss in the dehydroxylation region

Sample	Percentage loss		Percentage $2(H_2O)$
	(350–800 °C)	(d.w.)	
I Manito	3.91	4.49	4.22
II Sampor	3.96	4.46	4.19
III Polkville	4.68	5.44	4.73
IV Askangel	4.29	5.18	4.79
V J.P.	4.54	5.49	4.87
VI Bakony	4.40	5.13	4.75

Direct observation of the weight loss exhibited through dehydroxylation resulted in the data given in Table 1. These data indicate that the weight loss in this region lies within the stoichiometric release of two water molecules, as calculated for each structural formula ($\leq$ 12% higher). It is reasonable to

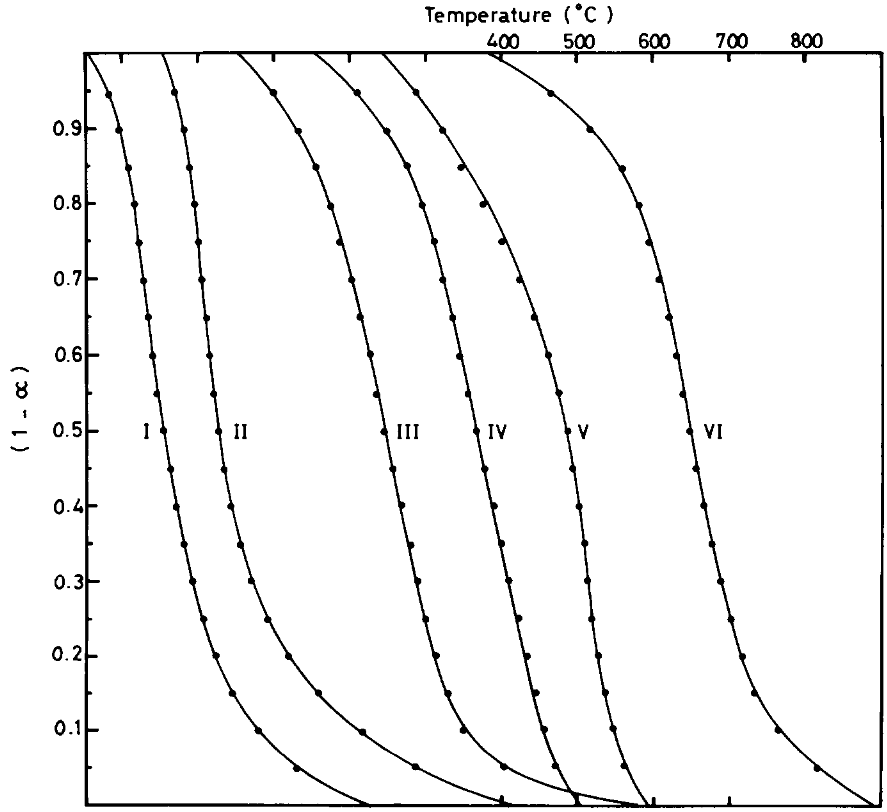

Fig. 1. Fractional decomposition curves of smectites in the dehydroxylation region.

infer from this that the tested solids represent typical nontronites and montmorillonites with respect to their chemical structures.

Derivation of kinetic parameters

The dehydroxylation weight loss traces were transformed into decomposition curves, presented in the form of undecomposed fraction $(1-\alpha)$ as function of temperature (Fig. 1). Analysis of the decomposition curves was carried out by applying four procedures. These are the first order equations described by Horowitz and Metzger [16], Coats and Redfern [17], Dave and Chopra [18], as well as the method outlined by Šatava and Škvara [19].

Method I: Horowitz and Metzger

These authors derived two general methods describing the shape of thermogravimetric traces governing first-order decompositions. In terms of the decomposed fraction, the corresponding expressions appear in the form:

$$\ln\ln\frac{1}{1-\alpha}=\frac{E_a\theta}{RT_s^2}\ \text{(Method }\mathbf{I}\text{)}\tag{1}$$

$$\text{and}\ \ln\ln\frac{1}{\alpha}=\frac{E_a\theta}{RT_s^2}\ \text{(Method }\mathbf{II}\text{)}\tag{2}$$

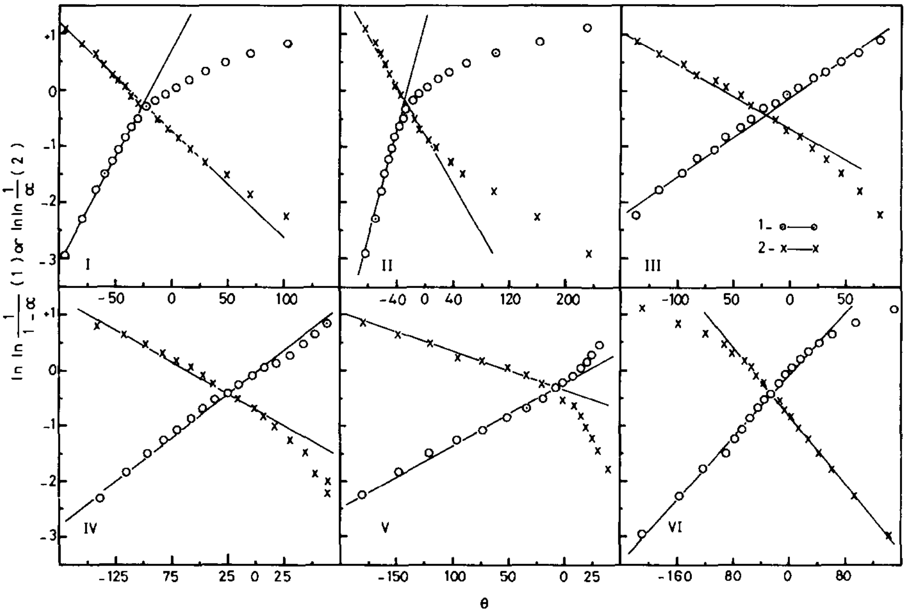

Fig. 2. Linear plots of Horowitz and Metzger: (⊙——⊙) Method **I**; (×——×) Method **II**.

TABLE 2

Activation energy of dehydroxylating smectites evaluated by the four methods

No. Parameter [a]	Horowitz and Metzger		Coats and Redfern	Dave and Chopra	Šatava and Škvara	log A
	Method I	Method II				
I E_a	40.53	22.75	35.70	36.30	35.05	9.19
α Range	0.05–0.50	0.05–0.75	0.05–0.50		0.05–0.60	
II E_a	46.94	26.37	39.56	39.80	38.63	11.64
α Range	0.05–0.50	0.05–0.60	0.05–0.45		0.10–0.50	
III E_a	25.21	14.38	16.84	17.37	22.34	3.64
α Range	0.05–0.85	0.05–0.65	0.05–0.60		0.05–0.70	
IV E_a	23.05	15.17	16.35	18.81	23.32	3.08
α Range	0.05–0.85	0.1 –0.60	0.05–0.95		0.05–0.80	
V E_a	17.38	16.82	8.82, 30.36	28.86	15.4, 34.8	0.88, 8.62
α Range	0.1 –0.65	0.05–0.45	0.10–0.45 0.50–0.95		0.05–0.40 0.40–0.95	
VI E_a	25.08	27.08	20.80	20.47	24.81	8.35
α Range	0.05–0.80	0.15–0.95	0.15–0.85		0.10–0.90	

[a] E_a values in kcal mol^{-1}.

where at T_s, the remaining fraction $(1-\alpha) = 1/e = 0.367$; $\theta = T_\alpha - T_s$; T_α, the temperature at the recorded fraction (α). From a plot of the appropriate left side vs. θ (Fig. 2), a straight line is obtained and from its slope the value of E_a could be evaluated (Table 2).

Method **I** seems better for montmorillonite as it covers more than 70% of the whole dehydroxylation range, whereas Method **II** is better for nontronite. In comparison to Method **II**, Method **I** always leads to higher (50–80%) values of activation energies. Only in the case of sample **VI**, do both methods evaluate almost the same value for E_a.

Method II: Coats and Redfern

The first-order expression appears in the form:

$$\log\left[\frac{\ln(1-\alpha)}{T^2}\right] = \log\frac{AR}{\beta E_a}\left(1-\frac{2R\bar{T}}{E_a}\right) - \frac{E_a}{2.3RT} \tag{3}$$

Thus upon plotting the left side of the above equation vs. $1/T$, the slope of the straight line obtained (Fig. 3) equals $-(E/2.3R)$, and the intercept equals:

$$\log\left[\frac{AR}{\beta E_a}\left(1-\frac{2R\bar{T}}{E_a}\right)\right] \tag{4}$$

Thus allowing the calculation of the activation energy E_a as well as the

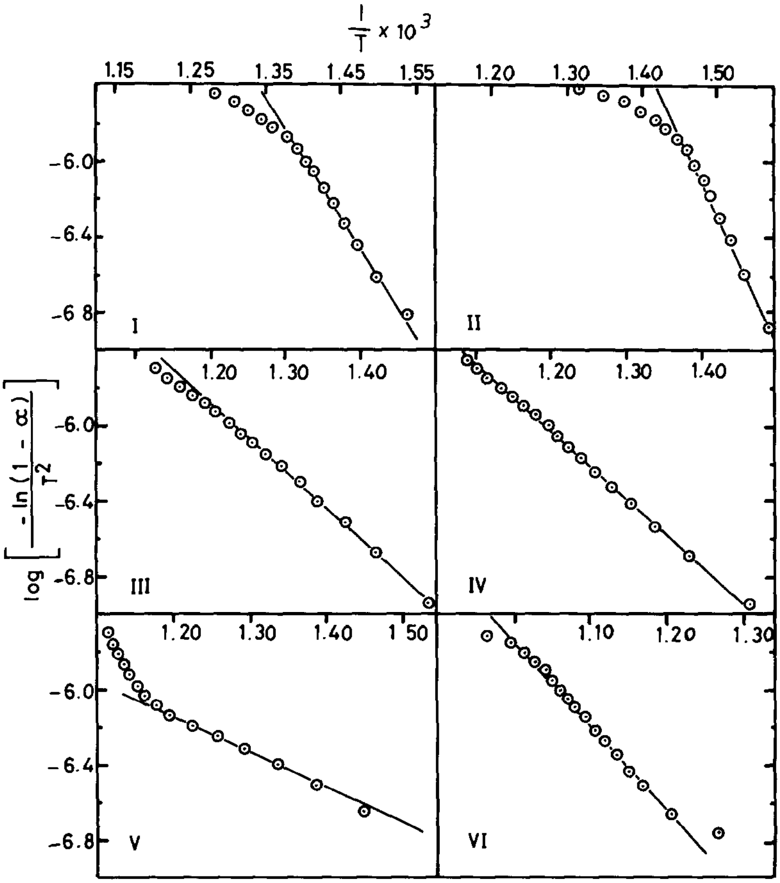

Fig. 3. First-order linear plots of Coats and Redfern.

preexponential term, A (β is the rate of heating). The temperature corresponding to 50% decomposition ($\bar{T}$) was used for the calculation of the latter parameter. The evaluated E_a and log A values are shown in Table 2.

The Coats and Redfern linear relationship covers a small fraction of decomposition when applied to the nontronites. It covers, generally, most of the dehydroxylation process of montmorillonites ($\geqslant$ 70%).

The method of Dave and Chopra

In this method the decomposition rate constant, $K_{(T)}$ is correlated to the total area under the differential thermogravimetric curve, A, area for the reaction up to time t, a, and height of the curve at temperature, T. For first-order reactions the given expression is

$$K_{(T)} = -\frac{\mathrm{d}\,\alpha}{\mathrm{d}\,t}/(A-a) \tag{5}$$

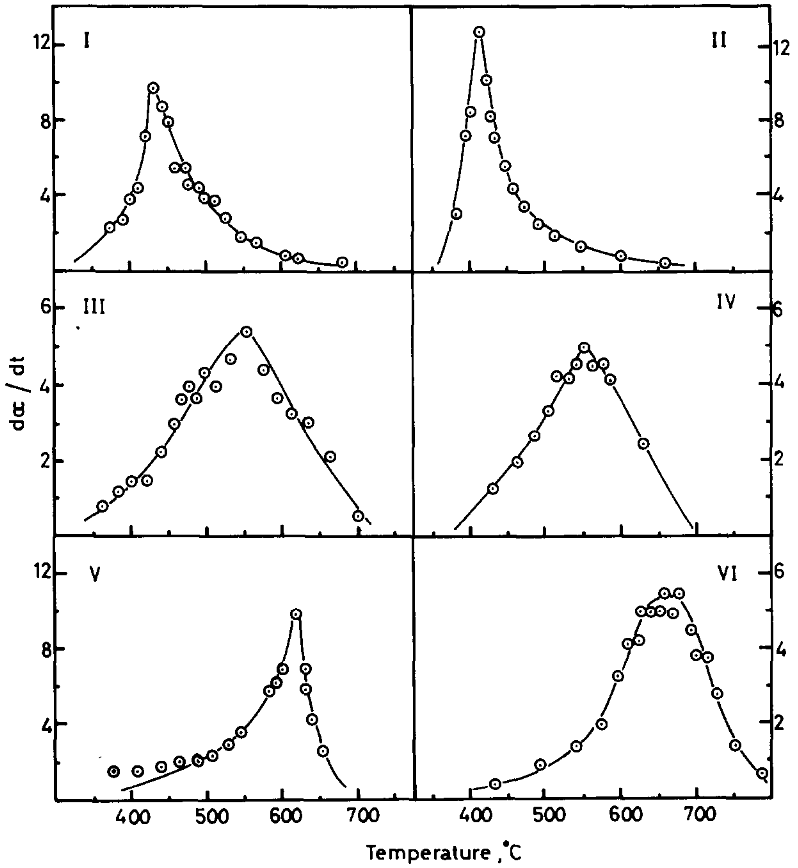

Fig. 4. Differential decomposition curves of smectites.

where $d\alpha/dt$ is the fraction decrease per degree, and $(A - a)$ is the residual area under the DTG curve (Fig. 4), both at the same temperature T. A plot of log k vs. $1/T$ yields a straight line whose slope equals $-(E/2.3\ R)$. This equation was claimed by the authors to be a simplified form of the tedious differential-difference method proposed by Freeman and Carroll [20]. The linear plots are shown in Fig. 5, and the evaluated activation energies are depicted in Table 2.

As noticed in the previous method, montmorillonites exhibit linear relationships up to high decompositions, whereas nontronites are limited to values before the maximum of the DTG curves.

The method of Šatava and Škvara

These authors selected ten functions, $g(\alpha)$, corresponding to specific reaction mechanisms pertaining to the thermal decomposition of solids. On plotting log $g(\alpha)$ for each of these rate processes vs. $1/T$, the most probably

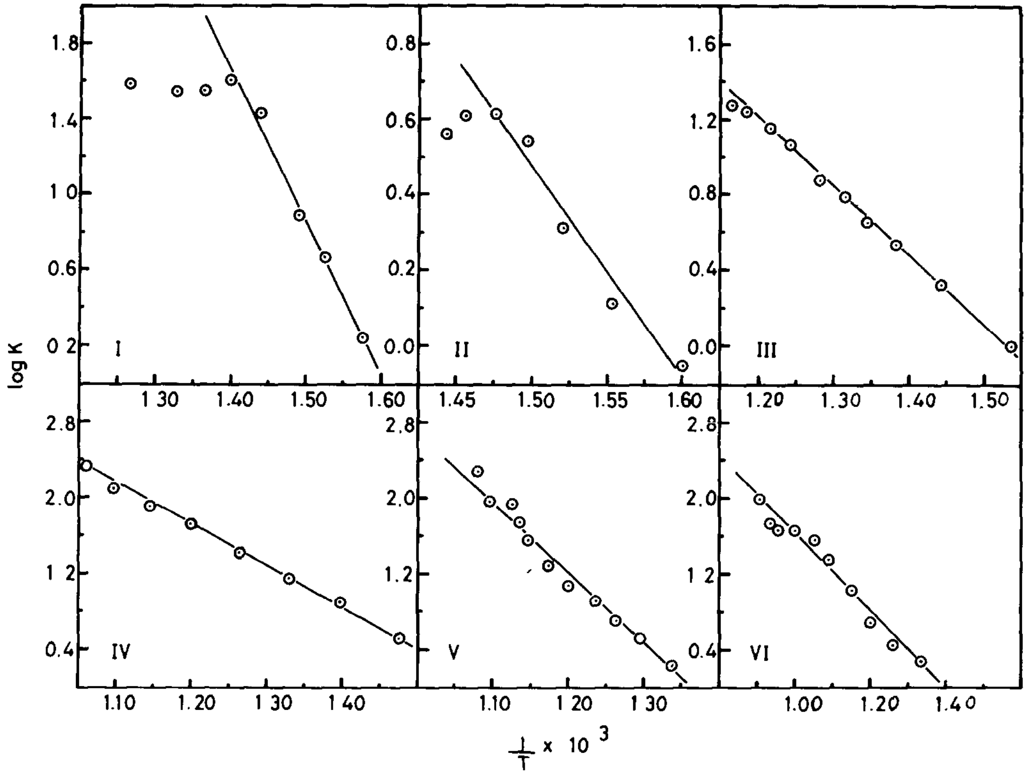

Fig. 5. Linear plots of Dave and Chopra.

predominant mechanism would yield a straight line extending over a wider range of α [21]. From its slope $tg\beta$, the activation energy can be evaluated from the approximated expression given by Šatava [21] and Šestak [22]

$$E_a = -tg\beta + \sqrt{tg^2\beta + 8tgB \cdot \bar{T}} \tag{6}$$

where $\bar{T}$ is the mean temperature corresponding to 50% decomposition.

Accordingly, the data of one sample (**II**) were tested and the best mechanism equation proved to be the unimolecular F_1 function. Then the log $g(\alpha)$ values corresponding to this function were plotted against $1/T_\alpha$ for all of the six samples under investigation. Satisfactory straight lines were observed extending to α values up to 0.90 in many cases (Fig. 6). The evaluated E_a are, likewise, included in Table 2.

DISCUSSION AND CONCLUSIONS

From a comparison of the above results it is clear that the materials under consideration are typically characteristic nontronites and montmorillonites.

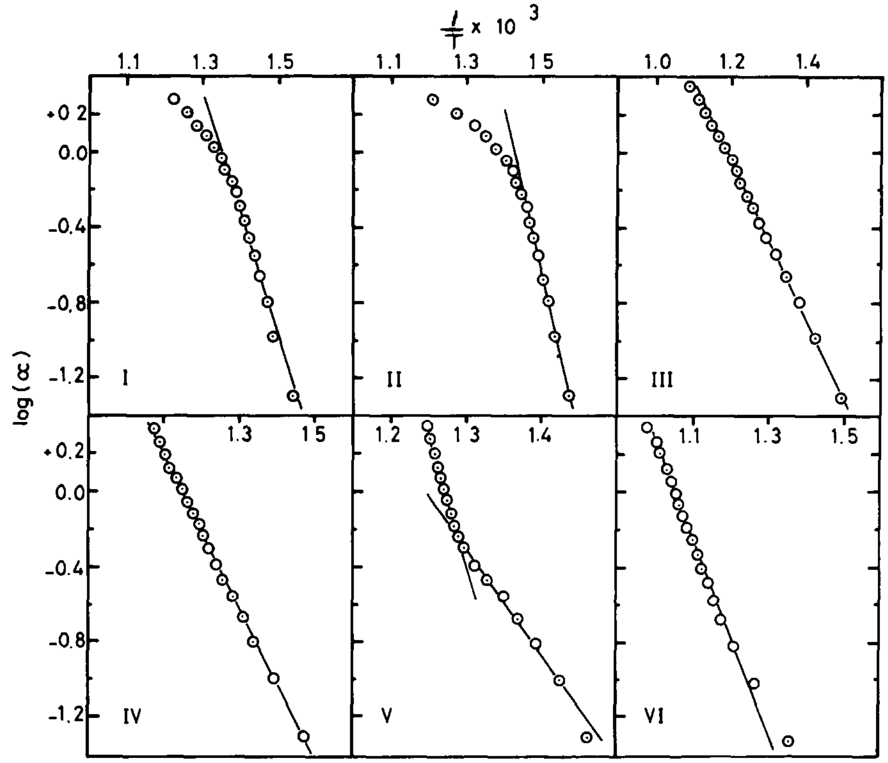

Fig. 6. Plots of log $g(\alpha)$ vs. $1/T$ for the F_1 function of Šatava and Škvara.

Thus, the change in weight loss appears as one continuous wave attaining slightly higher than the stoichiometric loss of two water molecules. However, in spite of the apparent structural similarity between each of the two varieties, nontronites and montmorillonites, every solid exhibits a decomposition curve different from the others. Nontronites, always, show a smaller induction period and a longer decay period (beyond 90% decomposition).

From the reasonably satisfactory straight line plots exhibited for most of the applied methods, it may be concluded that the dehydroxylation of the typical smectites under consideration is, in general, a first-order nucleation process independent of diffusional effects.

Excluding the low activation energies evaluated by Method **II** of Horowitz and Metzger, dehydroxylation of nontronites and montmorillonites is associated with mean activation energies of 39.1 and 21.8 kcal mol^{-1}, respectively. Dehydroxylation of nontronites display, in addition to the higher energies of activation, similarly higher pre-exponential factors, A. Montmorillonites are characterized, nevertheless, by widely different values of A (10^5-fold).

The increase in E_a seems to be accompanied by a respective increase in log A, a correlation referred to as the "compensation effect" [23], and recently employed as characterising each system investigated [24,25]. A least square straight line fit to the data in Table 2, as well as others to be presently published, of smectites is estimated and the linear "compensation effect" appears as

$$\log A = 0.389\,E_a - 4.639 \qquad (7)$$

Finally, it may be concluded that:

(1) The methods of Coats and Redfern, as well as of Dave and Chopra, lead to similar estimates of E_a ($\pm 10\%$), whereas the procedures of Horowitz and Metzger (Method I) and that Šatava and Škvara (F function) show likewise similar estimates of E_a. The latter methods calculate, in general, relatively higher values of activation energies.

(2) Dehydroxylation of the structural 4OH groups in nontronites is associated by higher values activation energies and Arrhenius constant, in comparison to montmorillonites.

(3) A first-order decomposition mechanism seems most probable as governing the dehydroxylation of smectites, although a relatively better fit to the TG traces holds for montmorillonites.

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