

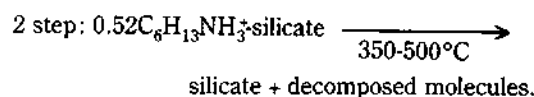
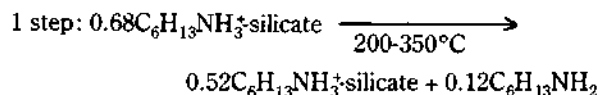
## Evaluation of Kinetic Parameters from Thermogravimetric Data of N-hexylammonium-Layer Silicate Intercalation Complex

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The applicability of kinetic models for nonisothermal studies on solid state reactions has received a great deal of attention in these years<sup>1-6</sup>. Many mathematical techniques and equations have been proposed which yield varying degrees of success.<sup>7</sup> One of these equations showing great applicability is that of Coats and Redfern.<sup>8</sup> This exhibits a good advantage since the reaction order and activation energy can be simultaneously calculated without much pre-knowledge of the sample.

In our previous works,<sup>9,10</sup> we have demonstrated the step-wise reaction pathway of the n-hexylammonium-layered silicate complexes according to the isomorphous substitution sites in the silicate lattice. Also, we have confirmed the first step is simple deamination, while the second is complicate decomposition including alkylchain cracking reaction, for which broensted acid catalysis mechanism has been proposed.



In this communication, we have done kinetic study only on the simple deamination step of the decomposition reaction because the alkylchain cracking process (second step) is not an elementary reaction, which makes a kinetic study impossible. For this purpose, we have employed Coats and Redfern method and carried out thermal analysis of the n-hexylammonium-layered silicate having layer charge of 0.68.<sup>9</sup> Dupont 1090 thermalanalyzer was adopted for this performance under nitrogen atmosphere with heating rate of 10°C/min.

The DSC, TG, and DTG thermograms for the sample are shown in Figure 1. The dehydration of interlayer water is identifiable as a separate step around 100°C. The step-wise decomposition of the sample can be seen in DTG curve. Though the two peaks are partly overlapped at 320-370°C, they can be considered as two individual peaks. The peak separation was performed on the basis of symmetry of the curves.<sup>8</sup> As a result, the approximate mole ratio of 0.23 to the total weight decrease was occurred in the first step, followed by the second step in which 0.77 mole ratio of intercalated n-hexylammonium cations are decomposed into smaller molecules. The decomposition of lattice hydroxy group was also monitored over 540°C.

The kinetic parameters for the simple deamination step (1 step) were determined by Coats and Redfern equation,

$$Y_n = \log \left\{ \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1 - n)} \right\} = \log \frac{AR}{aE} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.3RT}$$

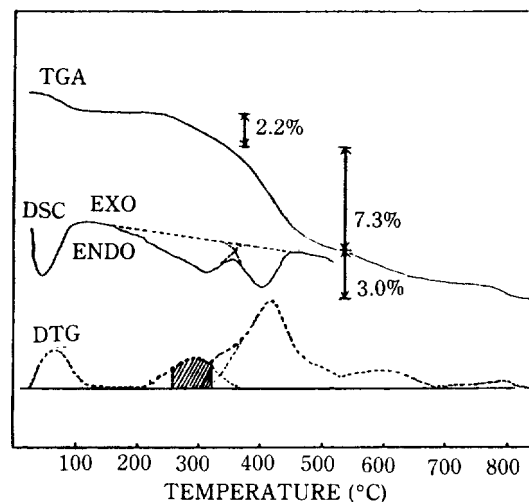


Figure 1. Thermogram of n-hexylammonium layer silicate. Heating rate: 10°C/min.

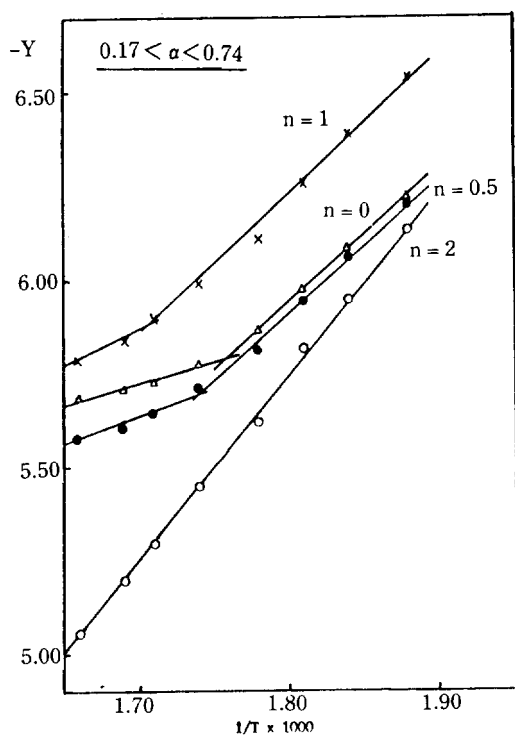
Table 1. Kinetic Data of the First Step

TEMP. (°C)	1/T × 1000 (K × 1000)	-Y <sub>n</sub> = 0	n = 0.5	n = 2/3	n = 1	n = 2
260	1.88	6.22	6.20	6.20	6.55	6.14
270	1.84	6.09	6.06	6.05	6.39	5.97
280	1.81	5.98	5.94	5.93	6.26	5.81
290	1.78	5.87	5.81	5.79	6.11	5.62
300	1.74	5.78	5.71	5.68	5.99	5.45
310	1.71	5.73	5.64	5.60	5.90	5.30
320	1.69	5.71	5.60	5.56	5.84	5.20
330	1.66	5.69	5.57	5.53	5.79	5.06
ACTIVATION ENERGY (kJ/mol)		47.4	56.5	60.4	67.8	95.3
CORRELATION COEFF.		0.977	0.986	0.987	0.992	0.999

in all cases except where n = 1. In that case

$$Y_n = \log \left\{ -\log \frac{(1 - \alpha)}{T^2} \right\} = \log \frac{AR}{aE} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.3RT}$$

was used. In these equations, E is the activation energy, T is the temperature (K). R is the gas constant, n is the reaction order, A is the pre-exponential factor, α is the fraction of reaction and a is the heating rate, which was held at 10°C/min. throughout this work. The intercept appears to be reasonably constant for most values of E and in the temperature range over which most reaction occur. The curve of each step was analyzed assuming n = 0, 1/2, 2/3, 1, and 2 to determine the reaction order and corresponding activation



**Figure 2.** Kinetic plots of simple deamination (1 step) with variation of reaction order  $n$ .

energies.<sup>8,11</sup> To avoid initiation and termination effects on the kinetics,<sup>8</sup> the range  $0.17 < \alpha < 0.74$  of the deamination step was investigated (see blocked area in Figure 1). The result of the numerical analysis is on Table 1, and plotted in Figure 2. The best fitting straight line is obtained by the second order ( $n=2$ ) equation with the correlation coefficient value of 0.999. With this equation, the activation energy of the deamination step is calculated as 95.3 kJ/mol. It is reasonable to consider that the intermediate of the deamination step involves the elongated state of N-H bond, which requires the

activation energy of 95.3 kJ/mol. According to the previously reported works,<sup>12,13</sup> the ammonium groups are oriented within the hexagonal siloxane hole on the interlayer surface of layered silicate, accompanied with weak N-H...O hydrogen bond. The N-O distance is reported to be at minimum 2.85 Å.<sup>13</sup> Therefore it can be concluded that the thermal energy of 95.3 kJ/mol is needed to disorient ammonium groups ionically bonded to the siloxane hole on the silicate and to break N-H...O hydrogen bond.

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## Internal Rotational Barriers of Ethyl Halides from SCF Calculations

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Dipole moments and barrier heights of internal rotations for ethyl halides ( $C_2H_5X$  where  $X=F, Cl, Br, I$ ) exhibit no apparent trends as halogen atom varies from fluorine to iodine. Values of dipole moments and internal rotational barriers are available from experiments<sup>1-5</sup>, but electronic structure calculations may provide detailed informations which are helpful in understanding these properties. In this report, we analyse the result of SCF calculations for ethyl halides with main emphasis on barrier heights of internal rotations. Many calculations on  $C_2H_5F$  and  $C_2H_5Cl$ , especially those at stable geometries, are available in the literature<sup>6-8</sup>, but none for

$C_2H_5Br$  and  $C_2H_5I$ . We perform SCF calculations for all ethyl halides with the similar basis sets in order to enhance the compatibility among calculated properties.

It is known that values of internal rotational barriers calculated with SCF method agree well with experiment even at SCF level when basis sets used in calculations are of reasonable size. Therefore, we employ 6-31G\* basis sets in ab initio SCF calculations for ethyl halides. In order to reduce the size of calculations and also to include relativistic effects, effective core potentials (ECP) of Hay and Wadt<sup>9</sup> are used for Cl, Br and I. The use of ECP is expected to introduce only