

The Thermal Decomposition and Hydrolysis of Calcium Carbamoyl Phosphate

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Calcium carbamoyl phosphate (**1**) was prepared by adding an aqueous calcium chloride solution to a reaction solution of KH_2PO_4 with KOCN . **1** was unstable at room temperature. **1** was dehydrated to make anhydrous salt and thermally decomposed to liberate ammonia, cyanic acid, and carbon dioxide, finally resulting in the formation of calcium pyrophosphate in air. The apparent activation energies for the three endothermic peaks of the DTA curve were estimated to be 50.0, 83.9, and 148.3 kJ mol^{-1} respectively. The hydrolysis of **1** in an aqueous solution apparently obeyed the first-order kinetics. The activation parameters for the hydrolysis of **1** were evaluated by using the ^{31}P NMR spectra of **1** with the lapse of the reaction time. The activation energy was 92.2 kJ mol^{-1} ; the activation enthalpy, 89.7 kJ mol^{-1} , and the activation entropy, -6.3 e.u.

Some phosphor-nitrogen compounds are already used as industrial materials and obtained as industrial products. There are a series of phosphorus-nitrogen compounds which have amino groups on a P atom. These compounds have the potential for use as new flameproofing and glow-retardant agents on a large number of cellulosic materials; further, they can be used as the starting materials in the preparation of many organic and inorganic phosphorus compounds.

In our previous papers,^{1–3)} the thermal behavior of many phosphoramidates were reported. This paper will describe the synthesis, thermal behavior, and hydrolysis of calcium carbamoyl phosphate (**1**) containing nitrogen and carbon. This compound was unstable even at room temperature, and its thermal product resulted in calcium pyrophosphate. It was found by ^{31}P NMR measurements that the hydrolysis of **1** apparently obeys the first-order kinetics.

Experimental

Preparation of Calcium Carbamoyl Phosphate. **1** was synthesized by reference to the method described in the literature.⁴⁾ Potassium dihydrogenphosphate (0.1 mol) and potassium cyanate (0.1 mol) were dissolved in 100 cm^3 of water. To the resulting mixture, which had been cooled in an ice bath, two solutions of 60 ml of 1 mol dm^{-3} BaCl_2 and 50 ml of 1 mol dm^{-3} NaOH were slowly added, drop by drop with continuous stirring. During the treatment, the pH of the solution was kept at 9.0–9.3. The resulting cream-colored precipitate of barium monohydrogenphosphate was removed by suction filtration. The filtrate was transferred to a flask, and 50 ml of 1 mol dm^{-3} CaCl_2 was added, drop by drop. To the resulting solution was slowly added 100 ml of ethanol. The resulting white precipitate was collected by suction filtration, washed with several small portions of water, ethanol, and acetone, air-dried, and finally dried in a vacuum over diphosphorus pentaoxide for 48 h.

Chemical Analysis. The phosphorus in a sample was determined colorimetrically by the molybdenum-blue method. The calcium in a sample was estimated by the atomic-absorption-analysis technique. The nitrogen, carbon, and hydrogen in a sample were determined by using a Hitachi C, H, N analyser-026 at the Toyama Medical and Pharmacy University.

Measurements. The thermal analysis measurements were made in air by using a Rigakudenki TG-DTA, DSC apparatus,

at the heating rates of 3, 5, 6, 8, and 10 K min^{-1} for TG-DTA and 5 K min^{-1} for DSC respectively. The IR spectra of the sample were recorded on a Nipponbunko IR-810 apparatus using the KBr-disc method. For the ^{31}P NMR spectra, a sample of about 100 mg was put in 5.0 cm^3 of a 6% EDTA deuterated-water solution and stirred for several minutes. A JNM-FX 90 Fourier transform spectrometer was used to measure the ^{31}P NMR spectra. An X-ray diffraction diagram of a powder sample was taken with nickel-filtered $\text{Cu K}\alpha$ radiation using a Shimadzu X-ray diffractometer XD-5, XD-3A, and a Rigaku RAD-RVB apparatus.

Results and Discussion

Thermal Behavior. The DTA and TG curves of **1** are shown in Fig. 1. The DTA curve indicated four endothermic peaks in this range: r.t.–362, 362–430, 430–465, and 465–541 K, while the TG curve indicated a slow decrease in the weight. For each type of peak (E_{D1} , E_{D2} , E_{D3} , and E_{D4}) shown in Fig. 1, two temperatures are recorded; the first one is the point of departure from the base line, while the second one is the end point of the peak temperature. The indication of “temperature” on the DTA curve in Fig. 1 means the temperature at which samples were removed from a furnace prior to being cooled in a silicagel desiccator and subjected to further research. The results of the elemental analyses of the thermal products are shown in Table 1. It can be seen from Table 1 that the nitrogen, carbon, and hydrogen contents of the thermal product decreased in the heating process and that the

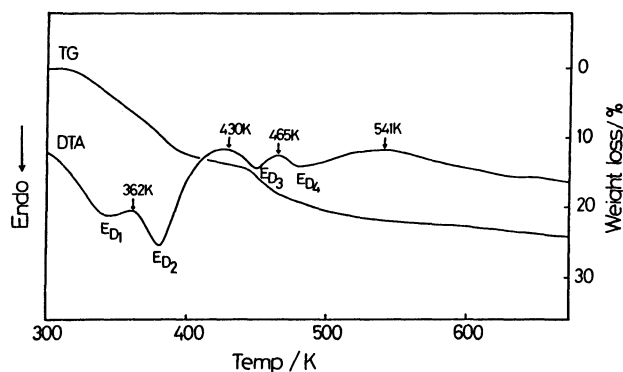


Fig. 1. DTA and TG curves of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$. Heating rate: 5 K min^{-1} .

thermal product at 541 K contained no nitrogen and hydrogen. These data on the reduction in weight after 30 min at each endothermic peak temperature were not always in agreement with those calculated from the TG curve. The results showed that carbon dioxide, ammonia, and cyanic acid are exhausted in the case of the thermal condensation of **1**.

The IR spectra of the thermal products are shown in Fig. 2. For the IR spectrum of **1**, the absorption band at about 3400 cm^{-1} is assigned to the N-H stretching vibration; those at 1680 and 1730 cm^{-1} , to the C=O stretching vibration; those at 1610 and 1630 cm^{-1} , to the N-H deformation vibration; that at 1400 cm^{-1} , to the C-N stretching vibration; that at 1150 cm^{-1} , to the P=O stretching vibration; that at 980 cm^{-1} , to the P-O-C stretching vibration, and that at 570 cm^{-1} , to the $(\text{PO}_2)^-$ or $(\text{PO}_3)^{2-}$ deformation vibration. These absorptions grew weaker with an increase in the temperature, and they disappeared in the thermal product at 430 K. At about 910 cm^{-1} , the absorption band attributed to the P-O-P antisymmetric stretching

Table 1. Elemental Analysis of the Thermal Products of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$

Sample	Ca/%	P/%	N/%	C/%	H/%
r.t. ^{a)}	19.1	15.0	6.2	5.4	2.3
	(19.4)	(15.0)	(6.8)	(5.8)	(2.5)
362 K	21.5	16.1	5.4	5.1	2.1
430 K	25.2	19.3	3.4	3.1	1.3
465 K	25.4	20.9	2.1	2.9	0.5
541 K	27.2	21.7	0.0	2.1	0.0
673 K	30.1	23.7	0.0	1.6	0.0
1273 K ^{b)}	32.5	24.5	0.0	0.0	0.0
	(32.8)	(25.4)			

a) Calculated values in parentheses as $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$.

b) Calculated values in parentheses as $\text{Ca}_2\text{P}_2\text{O}_7$.

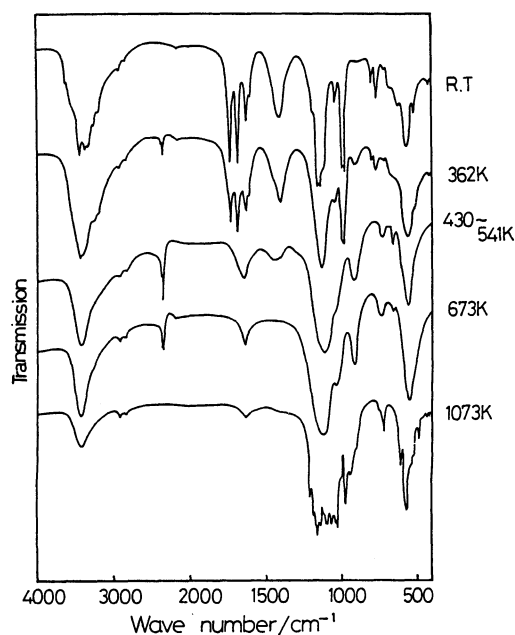


Fig. 2. IR spectra of the thermal products of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$.

vibration grew strong. This showed that the condensation polymerization was proceeding. For the thermal product at $362\text{--}673\text{ K}$, the absorption band of carbon dioxide was observed at 2350 cm^{-1} . Also, for the thermal product at 1073 K , the absorption observed at $900\text{--}1250\text{ cm}^{-1}$ was very complex, with strong peaks. This complexity of absorption was attributed to the progress of the crystallization.

The ^{31}P NMR spectra of the thermal products are shown in Fig. 3. As has been mentioned previously, **1** is very instable at room temperature; therefore, the

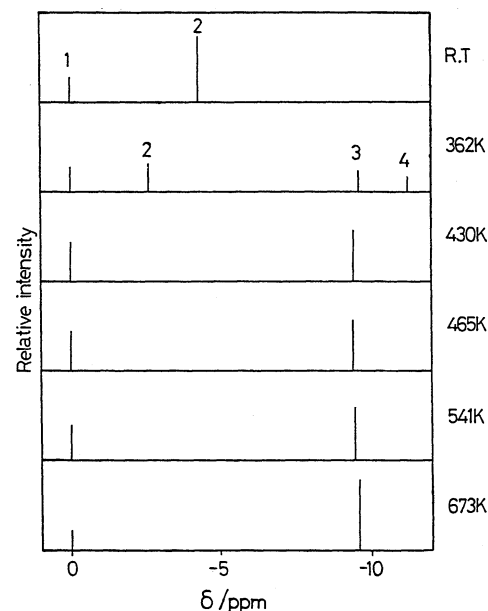


Fig. 3. ^{31}P NMR spectra of the thermal products of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$. 1: Orthophosphate, 2: carbamoylphosphate, 3: diphosphate, 4: end PO_4 group of intermediate polyphosphate ($n > 3$).

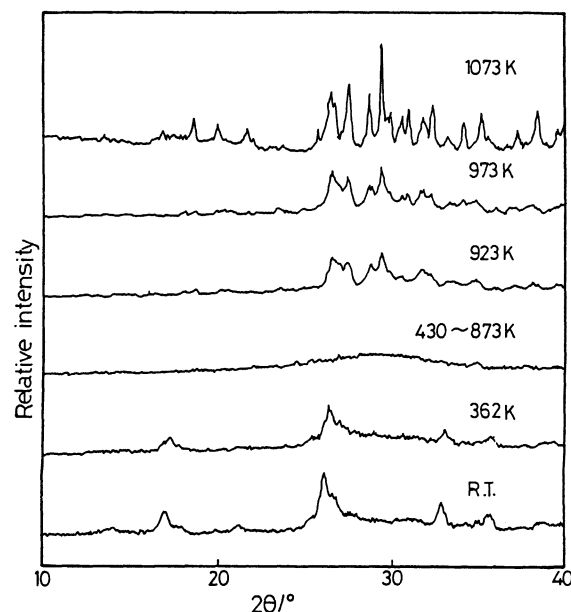


Fig. 4. X-Ray diffraction diagrams of the thermal products of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$. Heating rate: 2 K min^{-1} .

^{31}P NMR spectrum of **1** indicated peaks caused by a carbamoyl phosphate (CAP) and an orthophosphate (PO_4). The molar ratio $\text{CAP}/(\text{CAP}+\text{PO}_4)$, is calculated by means of the signal area, was 0.88 for **1**. The ^{31}P NMR spectrum of the thermal product at 362 K indicated peaks attributable to a PO_4 , a CAP, a diphosphate (P_2O_7), and an intermediate of the thermal condensation. The thermal product at 430 K indicated no CAP peak, but peaks of PO_4 and P_2O_7 were both registered. These results agreed with those of the IR spectra. The peak of P_2O_7 grew stronger above 430 K.

The X-ray diffractions of the thermal product at a given isothermal temperature, as obtained by using XD-3A, are shown in Fig. 4. No diffraction patterns on the thermal products were observed at room temperature at 430–873 K. The X-ray diffraction of the thermal product at 973 K indicated weak patterns, but these patterns were much clearer than those at 923 K. The X-ray diffraction patterns of the thermal products at the temperature interval from 465 to 673 K, as obtained using the Rigaku RAD-RVB apparatus, were similar to the amorphous solid compositions, as is shown in Fig. 4. The thermal product at 1073 K showed strong X-ray diffraction patterns of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$.⁵⁾

Decomposition at Room Temperature. The stability of **1** was checked at room temperature (283–303 K) in air. Figure 5 should the IR and ^{31}P NMR spectra of the decomposition of **1** at room temperature. **1** was very instable at room temperature. At 910 cm^{-1} , the absorption of the P–O–P antisymmetric stretching vibration appeared, and its intensity increased with the lapse of the reaction time. Therefore, either the polymerization or the condensation of **1** seemed to be progressing. This agrees with the results of the IR and ^{31}P NMR spectra. A peak attributable to P_2O_7 appeared after the lapse of 8 days, and its intensity increased with the lapse of the reaction time. A peak due to CAP decreased with the lapse of the reaction time. A peak due to CAP decreased with the lapse of

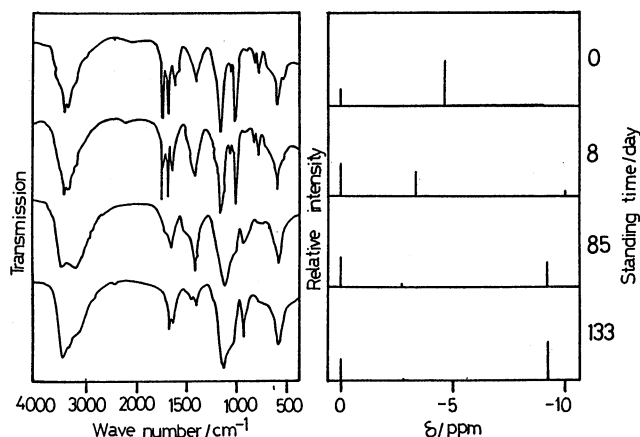


Fig. 5. IR and ^{31}P NMR spectra of the decomposition of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$ at room temperature.

the reaction time, on the other hand, and disappeared at 133 days.

Kinetic Studies of Thermal Process. Kinetic studies of the pyrolysis (i.e., dehydration and condensation) of **1** were done by the Kissinger method⁶⁾ on the basis of the DTA peaks E_{D1} – E_{D4} , as is shown in Fig. 1. As the heating rate increased, both the initial transition and the peak maximum for dehydration and condensation were shifted to higher temperatures. The theoretical work of Kissinger indicated that the activation energy of the pyrolysis process of **1** was defined by the following form:

$$\frac{d \ln(\phi/T_m^2)}{d(1/T_m)} = -E/R$$

where ϕ stands for the heating rate; T_m , for the temperature of the DTA-maximum, E , for the activation energy, and R , for the gas constant. These plots of $\ln(\phi/T_m^2)$ against $1/T_m$ are linear, the slope being equal to $-E/R$. Thus, the apparent activation energies of each pyrolysis process were obtained from this slope. The apparent activation energies for the three endothermic peaks ($=E_{D1}$, E_{D2} , and E_{D3}) were estimated to be 50.0, 83.9, and 148.3 kJ mol^{-1} respectively. The results are shown in Fig. 6 and Table 2. As the heating rate increased, the peak maximum for E_{D4} was not appreciably shifted. It was found that the E_{D4} peak was caused by the heat of crystallization.

According to these results, the pyrolysis mechanism of **1** may be written as Scheme 1. **1** is dehydrated to

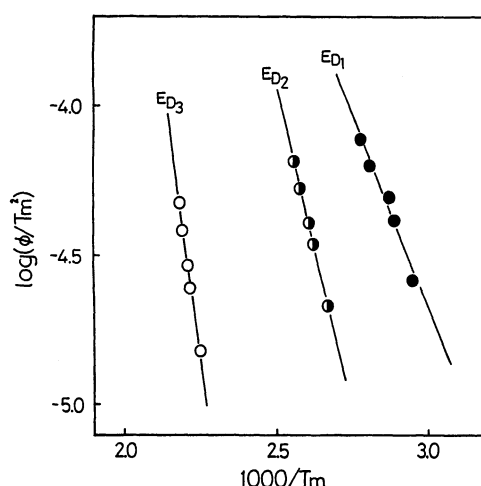
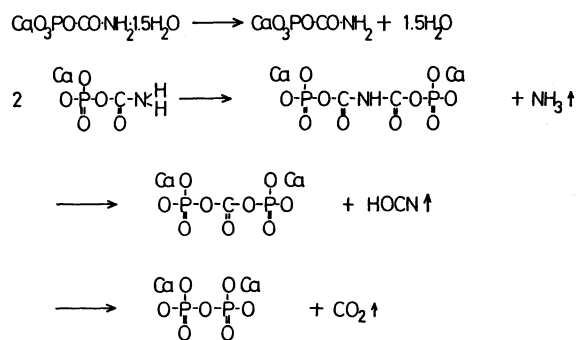


Fig. 6. The Kissinger's plots for E_{D1} , E_{D2} , and E_{D3} in DTA curves for $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$.

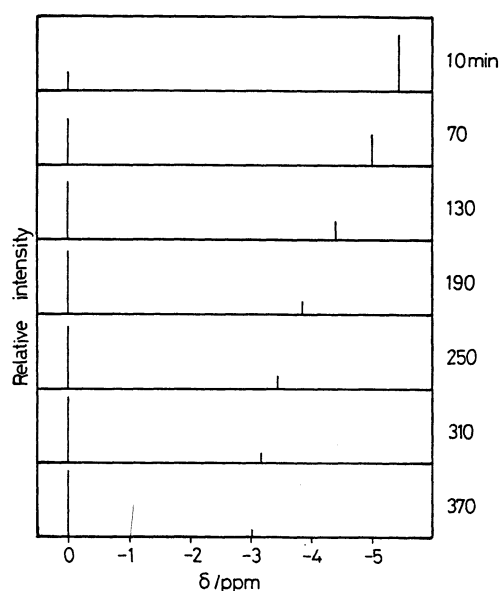
Table 2. Kinetic Data for the Pyrolysis of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$

DTA peak	Equation of straight line	$r^{(1)}$	$E/\text{kJ} \cdot \text{mol}^{-1}$
E_{D1}	$\log(\phi/T_m^2) = -2.609 \cdot 1000/T_m + 3.147$	0.985	50.0
E_{D2}	$\log(\phi/T_m^2) = -4.378 \cdot 1000/T_m + 7.019$	0.996	83.9
E_{D3}	$\log(\phi/T_m^2) = -7.735 \cdot 1000/T_m + 12.550$	0.999	148.3

a) Linear correlation coefficient.

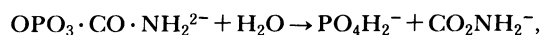


Scheme 1.

Fig. 7. ^{31}P NMR spectra of $\text{CaCAP}\cdot 1.5\text{H}_2\text{O}$ with the elapse of the reaction time at 302.6 K.

make anhydrous salts. Next, the anhydrous salts are bimolecularly condensed to liberate ammonia, cyanic acid, and carbon dioxide. Finally, calcium pyrophosphate is formed.

Hydrolysis of Calcium Carbamoyl Phosphate in an Aqueous Solution. The hydrolysis of **1** in an aqueous solution seems to progress as follows:

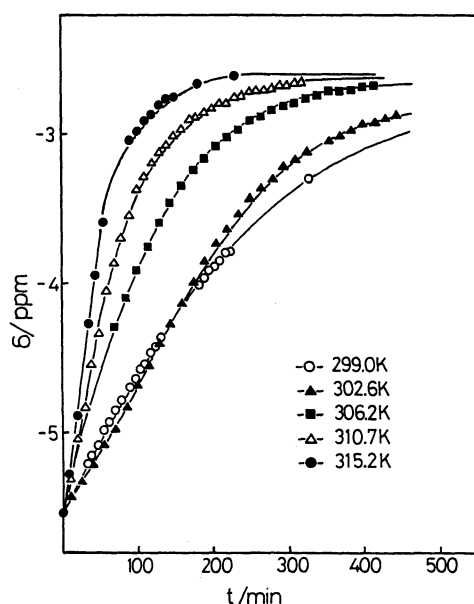
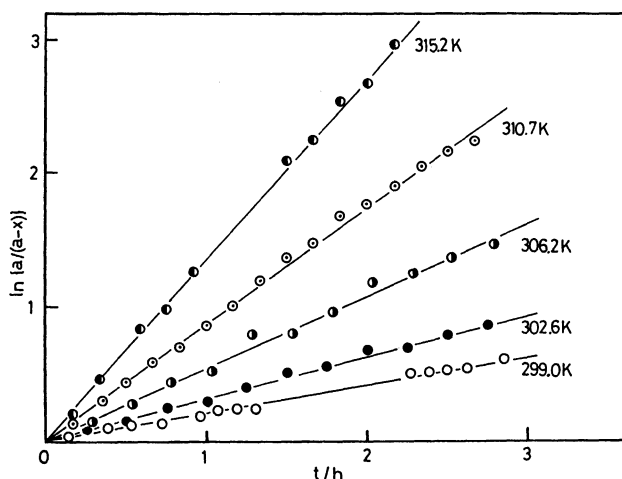


^{31}P NMR measurement was used to investigate the hydrolysis reaction of **1** at temperatures from 299.0 to 315.2 K. The ^{31}P NMR spectra of **1** with the lapse of the reaction time at 302.6 K are shown in Fig. 7. These spectra indicated peaks attributable to CAP and PO_4 ; the former decreased and shifted to a low magnetic field with the lapse of the reaction time. The chemical shifts of the ^{31}P NMR spectra at various temperatures, taken at intervals, are shown in Fig. 3. Smooth curves were obtained at all temperatures. The speed of shifting grew rapidly with the rise in the temperature. After the lapse of an infinite time, the peak due to CAP

was shifted by about -2.6 ppm. This phenomenon is independent of the pH, as was shown in the pH measurement of a solution⁷⁾ with the lapse of the reaction time over a period of 307 min. As Fig. 7 shows, the peak attributable to CAP decreased and that attributable to PO_4 increased with the lapse of the reaction time (apparently obeying the first-order kinetics). The first-order kinetics can be represented as follows:

$$kt = \ln \frac{a_0 - a_\infty}{a_t - a_\infty},$$

where a_0 and a_∞ are the CAP/(CAP+ PO_4) molar ratios at the beginning and when the reaction is complete respectively; a_t , the value after time t , and k , the rate constant. a_0 , a_∞ , and a_t were determined by measuring the integral intensities of the ^{31}P NMR spectrum for CAP and PO_4 respectively. The first-order kinetic

Fig. 8. The chemical shift of ^{31}P NMR spectra at various temperatures.Fig. 9. The first order kinetic plots of $\ln a/(a-x)$ vs. t for the hydrolysis of $\text{CaCAP}\cdot 1.5\text{H}_2\text{O}$ in aqueous solution.

plots of $\ln[(a_0 - a_\infty)/(a_t - a_\infty)]$ vs. t at various temperatures were found to be linear, as is shown in Fig. 9. The rate constants for the hydrolysis of **1** are shown in Table 3. Arrhenius plots (Fig. 10) give us the activation energy and the frequency factor. The activation enthalpy and entropy were obtained by using the values of the activation energy and the frequency factor. These kinetic data are tabulated in Table 4.

One of the most significant treatments of the theory of reaction rates is based on the concept of the existence of an activated complex as an intermediate stage in all chemical reactions. In a reaction involving two

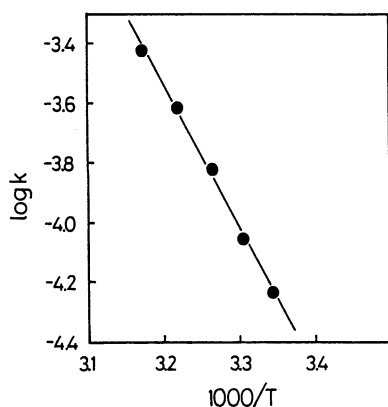


Fig. 10. Arrhenius plots of the first order rate constants for the hydrolysis of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$ in aqueous solution.

Table 3. Rate Constants for the Hydrolysis of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$ in an Aqueous Solution

T/K	Rate constant k/s^{-1}	$r^{(1)}$
299.0	5.82×10^{-5}	0.997
302.6	8.83×10^{-5}	0.998
306.2	1.51×10^{-4}	0.996
310.7	2.42×10^{-4}	0.999
315.2	3.78×10^{-4}	0.999

a) Linear correlation coefficient.

Table 4. Kinetic Data for the Hydrolysis of $\text{CaCAP} \cdot 1.5\text{H}_2\text{O}$ in an Aqueous Solution

$A/\text{s}^{-1} \text{mol}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{e.u.}$
7.02×10^{11}	92.2	89.7	-6.3

or more molecules, the reactants, possessing sufficient energy, must approach one another closely. Since in any bimolecular reaction except in the dissociation of two molecules, a reaction with $A \approx 10^{11} \text{M}^{-1} \cdot \text{s}^{-1}$ is generally regarded as a standard bimolecular reaction,⁸⁾ the value of the frequency factor in this paper suggests a bimolecular reaction. Even in a unimolecular reaction, in which a single molecule takes part in each chemical act, it is necessary for some rearrangement of atoms and energy to occur, thus giving the requisite activated complex, before a reaction can take place. From the results of Table 4, the value of the activation energy can be said to be approximately identical to that of the activation enthalpy. By supposing that an equilibrium exists between the reacting molecules and the activated complex, which decompose at a definite rate, it has been found possible to estimate the apparent $\Delta S^\ddagger$ value for the hydrolysis reaction. Such a $\Delta S^\ddagger$ value suggests that mechanism of the hydrolysis reaction consists of two main complicating steps which can be described by the above chemical equations.

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