On the Reactivity of Amide Group of ε-Caprolactam Derivatives

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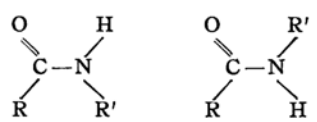
The bond between carbon and nitrogen of an amide has appreciably double bond character due to resonance[1], and the configuration of amide linkage tends to be a planer structure and two configurations of *cis* and *trans* forms are possible as follows:



cis form *trans* form

ε-Caprolactam is the *cis* form[2], while monosubstituted acid amide RNHCOR′ is the *trans* form[3]. It was ascertained[4] that ε-caprolactam caused an amide interchange reaction with a *trans* amide and the reaction rate of ε-caprolactam with its ring oligomers became faster with the enlargement of the ring. When it is compared with the polymerization of ε-caprolactam, the equilibrium between ring and chain structures shifts to the ring form in the case of the polymerization of substituted ε-caprolactam such as γ-methyl-ε-caprolactam, and *N*-methyl-ε-caprolactam is too stable to polymerize[5]. Therefore, this study was undertaken in order to elucidate the difference in reactivity of amide group of ε-caprolactam derivatives.

1) G. W. Wheland, "Resonance in Organic Chemistry", John Wiley & Sons, Inc., New York (1955), p. 109.
2) M. Tsuboi, This Bulletin, **22**, 215 (1949).
3) S. Mizushima et al., *J. Am. Chem. Soc.*, **72**, 3490 (1950).
4) N. Ogata, Contributed to the *Makromoleculare Chemie*.
5) H. Yumoto, K. Ida and N. Ogata, This Bulletin, **31**, 249 (1958).

Experimental

1. Determination of the Dipole Moment of Amides.—The dipole moment of ε-caprolactam, γ-methyl-ε-caprolactam and *N*-methyl-ε-caprolactam was determined in benzene solution at 25°C, as shown in Table I. The molecular polarization of ε-caprolactam or γ-methyl-ε-caprolactam decreased with the increase of the concentration but that of *N*-methyl-ε-caprolactam was almost constant, as shown in Fig. 1.

TABLE I. THE DIPOLE MOMENT OF ε-CAPROLACTAM DERIVATIVES

Sample	Dipole moment (D)
ε-Caprolactam	3.88
γ-Methyl-ε-caprolactam	5.48
N-Methyl-ε-caprolactam	4.23

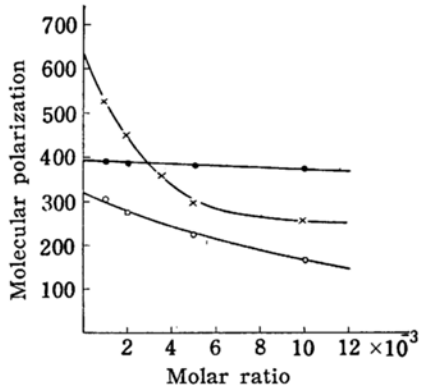


Fig. 1. The molecular polarization of ε-caprolactam derivatives.
● *N*-Methyl-ε-caprolactam
× γ-Methyl-ε-caprolactam
○ ε-Caprolactam

TABLE II. THE RATE OF HYDROLYSIS OF ε-CAPROLACTAM

Temp. (°C)	Concn. of H_2SO_4 (N)	Reaction time (hr.) 1/6	1/3	1/2	1	2	3	5	7	8
60	1.0	—%	—%	—%	4.9%	6.7%	11.4%	15.1%	21.2%	—%
60	2.0	—	—	—	8.2	12.9	19.4	32.7	42.9	—
80	1.0	—	—	13.1	21.0	34.7	43.3	59.5	67.1	—
80	2.0	10.9	15.0	16.0	38.0	56.9	78.9	88.0	—	—
100	0.5	—	—	24.9	40.8	49.2	56.1	63.3	—	—
100	1.0	21.7	32.9	44.9	66.3	87.3	93.2	97.5	—	100.0
100	1.5	28.2	56.8	60.2	80.6	100.0	—	—	—	—
100	2.0	35.3	60.2	64.7	86.5	100.0	—	—	—	—

TABLE III. THE RATE OF HYDROLYSIS OF RING OLIGOMERS
(Concentration of sulfuric acid, 3 N)

Ring oligomer	Temp. (°C)	Reaction time (hr.) 2	4	6	8	10	15	20
dimer	78	—%	—%	—%	5.2%	—%	8.8%	12.0%
	100	—	6.8	9.7	—	21.6	29.6	25.5
trimer	78	—	6.1	8.4	12.4	—	—	—
	100	18.0	32.0	38.0	42.3	—	—	—
tetramer	78	—	5.4	7.7	11.9	—	—	—
	100	20.0	28.5	34.0	39.0	—	—	—

TABLE IV. THE RATE OF HYDROLYSIS OF *N*-METHYL-ε-CAPROLACTAM

Temp. (°C)	Concn. of H_2SO_4 (N)	Reaction time (hr.) 1	2	3	4	5	7.5	10	15	20	30
80	3.0	1.8%	4.4%	6.3%	—%	12.9%	15.5%	18.5%	—%	—%	—%
90	3.0	—	10.2	—	17.2	21.7	31.5	40.1	—	—	—
100	1.0	9.4	16.0	19.7	24.0	27.6	—	40.3	—	—	—
100	2.0	10.8	18.0	27.4	34.9	40.5	—	60.8	—	—	—
100	3.0	12.3	23.5	30.3	36.5	43.9	57.6	67.9	75.8	82.2	89.8
100	5.0	8.4	18.0	26.1	38.6	46.7	—	100.0	—	—	—

2. Determination of the Reaction Rate of Hydrolysis.—ε-Caprolactam, *N*-methyl-ε-caprolactam or ring oligomers of ε-caprolactam which were obtained by repeated recrystallizations of the water extract of poly-ε-capramide, at the amount of 10^{-2} mol., was heated in 20 ml. of sulfuric acid in sealed glass tubes and then the solution was neutralized quickly. The quantities of ε-aminocaproic acid formed in the case of ε-caprolactam or its ring oligomers could be determined by the formol titration method but the quantitative determination of *N*-methyl-ε-aminocaproic acid was possible by neither the formol titration nor the method using an ion exchange resin. *N*-methyl-ε-aminocaproic acid could be quantitatively determined in the mixed solvent of ethanol and 30% formalin (1:1). The neutralized solution of *N*-methyl-ε-aminocaproic acid was filled up to 50 ml. and 10 ml. of the solution were dried and then the residue was dissolved in 10 ml. of ethanol and 30% formalin. The solution was titrated by 0.1 N sodium hydroxide solution with phenolphthalein as an indicator. These results are shown in Tables II, III and IV.

The hydrolysis of lactam in the presence of large quantities of water is the first order reaction and the rate constant is calculated by the following equation, where a designates the mole of amide and x the mole of amino acid formed at t hr.

$$k=2.303/t\cdot\log\, a/(a-x) \qquad (1)$$

The rate constants, which are shown in Table V, are proportional to the concentration of sulfuric acid, as shown in Figs. 2 and 3.

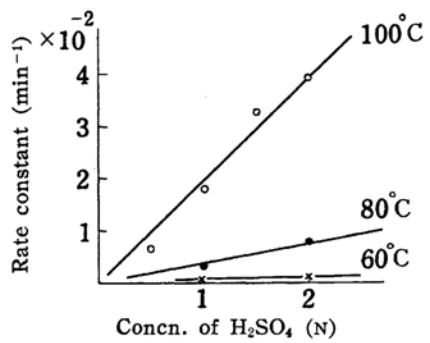


Fig. 2. The rate constant of hydrolysis of ε-caprolactam.

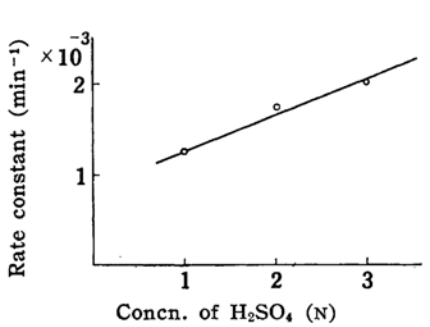


Fig. 3. The rate constant of hydrolysis of *N*-methyl-ε-caprolactam at 100°C.

TABLE V. THE RATE CONSTANT OF HYDROLYSIS OF ε-CAPROLACTAM DERIVATIVES

Sample	Temp. (°C)	Concentration of H_2SO_4 (N)	Rate constant (min^{-1})
ε-Caprolactam	60	1.0	0.6×10^{-3}
		2.0	1.3×10^{-3}
	80	1.0	3.5×10^{-3}
		2.0	8.0×10^{-3}
	100	0.5	6.4×10^{-3}
		1.0	18.1×10^{-3}
		1.5	33.2×10^{-3}
		2.0	39.4×10^{-3}
N-Methyl-ε-caprolactam	80	3.0	0.38×10^{-3}
	90	3.0	0.84×10^{-3}
	100	1.0	1.23×10^{-3}
		2.0	1.73×10^{-3}
		3.0	2.00×10^{-3}
Ring dimer	78	3.0	0.11×10^{-3}
	100	3.0	0.25×10^{-3}
Ring trimer	78	3.0	0.26×10^{-3}
	100	3.0	1.15×10^{-3}
Ring tetramer	78	3.0	2.33×10^{-3}
	100	3.0	13.75×10^{-3}

3. Determination of Infrared Spectrum.—The infrared spectrum of ε-caprolactam, ring-dimer, -trimer and -tetramer, which is shown in Figs. 4, 5, 6 and 7, was measured in a potassium bromide disc with a Hitachi model EPI-2 spectrophotometer, with a rock-salt prism. The absorption band of N-H of ε-caprolactam appears at 3215 and 3077 cm^{-1}, while that of ring-dimer at 3279 and 3077 cm^{-1}. The absorption band of CO of ε-caprolactam appears at 1650 cm^{-1}, while that of ring-dimer at 1639 cm^{-1}. The spectrum of ring-dimer shows absorption maximum at 1555 cm^{-1}, which is not found in ε-caprolactam. The absorption bands of N-H of ring-trimer and -tetramer appear at 3289 and 3077 cm^{-1} and the spectra come to resemble that of poly-ε-capramide (Fig. 8).

When dry hydrogen chloride was introduced into carbon tetrachloride solution of ε-caprolactam, a white crystal was precipitated. This crystal was decomposed easily in the air, evolving hydrogen chloride. It was filtered off in dry hydrogen chloride atomosphere and dried, and then its infrared spectrum was measured, in a potassium bromide disc, which is shown in Fig. 9. The absorption bands of N-H at 3215 and 3077 cm^{-1} disappear and new ones appear at 2730, 2500 and 2398 cm^{-1}. The absorption band of N-H of dibutylamine $(C_4H_9)_2N$-H appears only at 3311 cm^{-1}, while that of its hydrochloride at 2564, 2463 and 2398 cm^{-1}. Therefore, these new bands are estimated to be the absorption of N-H of the reaction product which was produced by adding hydrogen chloride to the nitrogen atom of ε-caprolactam. The absorption band of CO of the

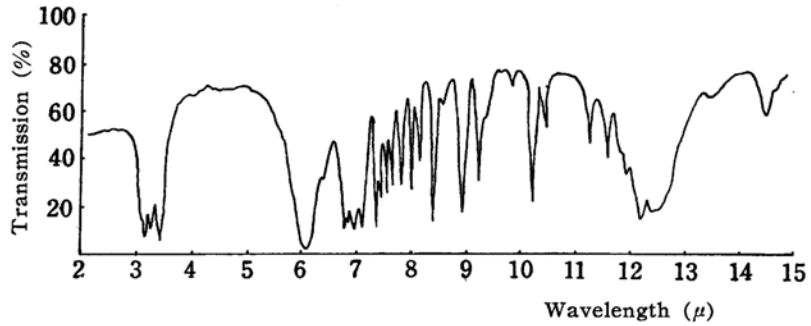


Fig. 4. The infrared spectrum of ε-caprolactam (KBr disc).

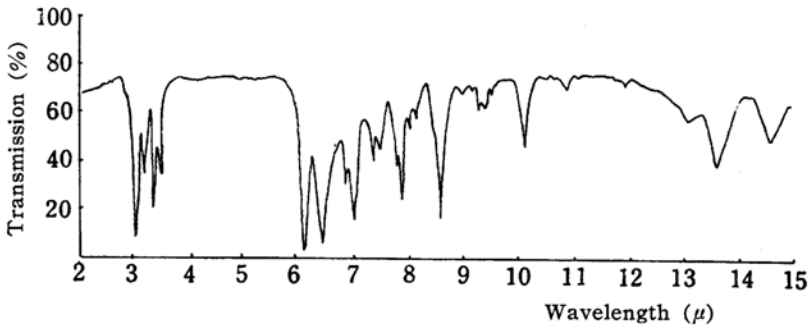


Fig. 5. The infrared spectrum of ring dimer (KBr disc).

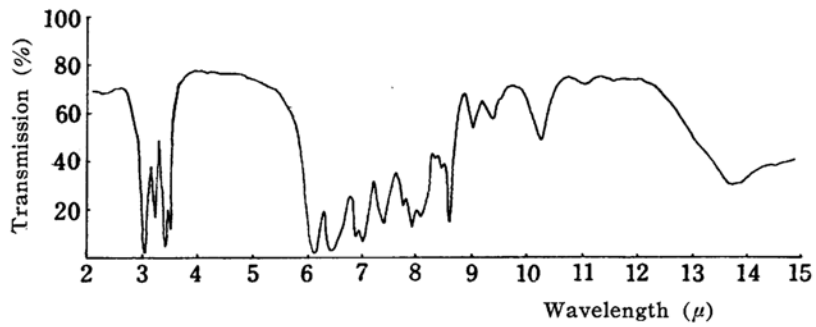


Fig. 6. The infrared spectrum of ring trimer (KBr disc).

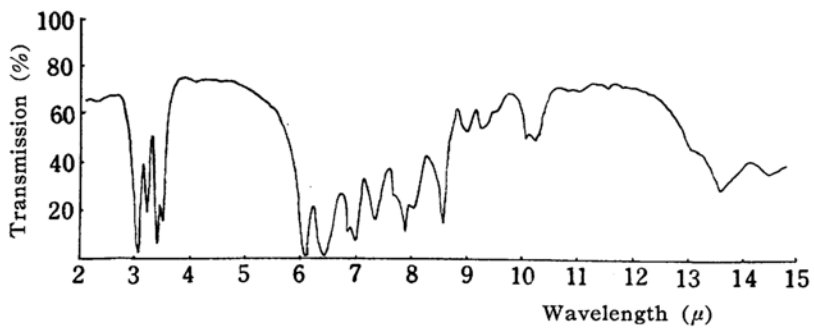


Fig. 7. The infrared spectrum of ring tetramer (KBr disc).

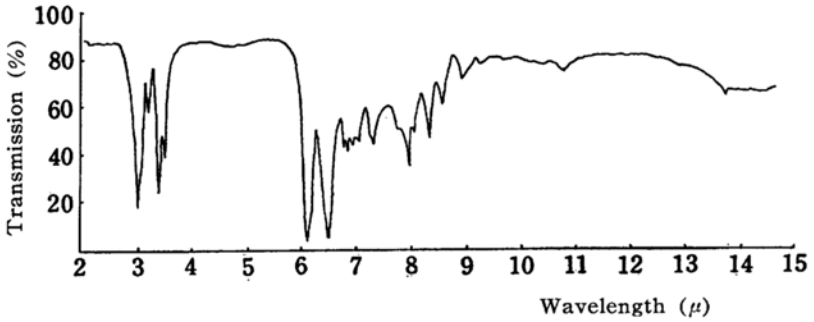


Fig. 8. The infrared spectrum of poly-ε-capramide (KBr disc).

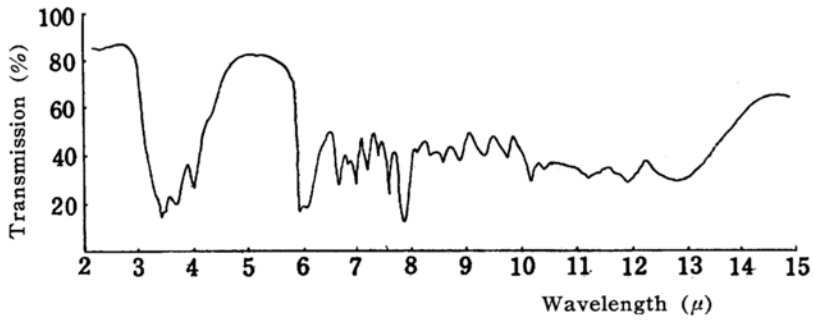


Fig. 9. The infrared spectrum of the reaction product of ε-caprolactam with hydrogen chloride (KBr disc).

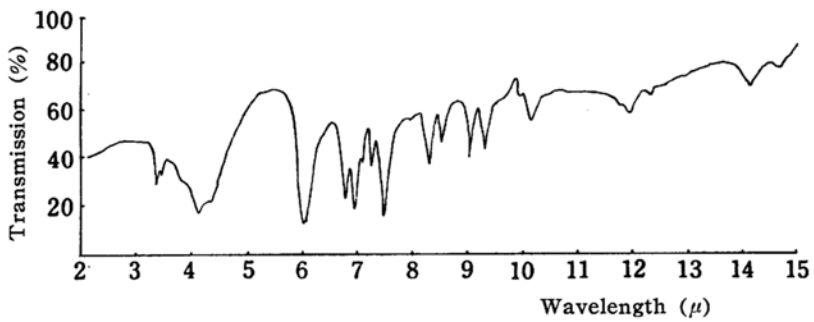


Fig. 10. The infrared spectrum of the reaction product of *N*-methyl-ε-caprolactam with hydrogen chloride (KBr disc).

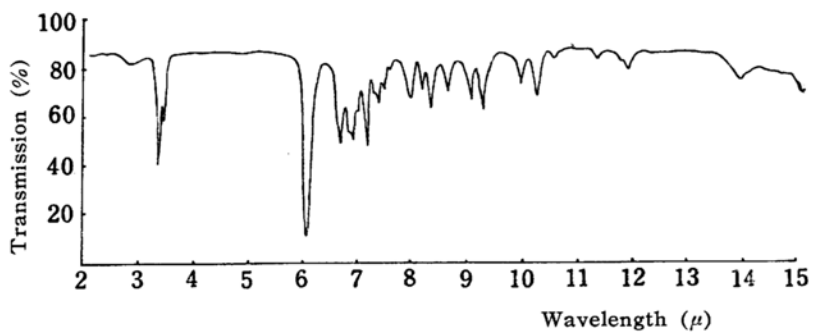


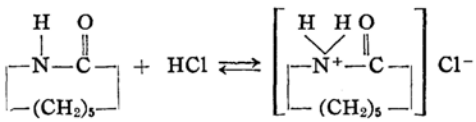
Fig. 11. The infrared spectrum of *N*-methyl-ε-caprolactam (liquid).

reaction product shifts from 1650 to 1681 cm^{-1}.

When dry hydrogen chloride was introduced into carbon tetrachloride solution of *N*-methyl-ε-caprolactam, a white crystal was precipitated but it dissolved again by the further introduction and *N*-methyl-ε-caprolactam was floated on carbon tetrachloride. The infrared spectrum of the crystal formed at first was measured in a potassium bromide disc, which is shown in Fig. 10. A new broad absorption appears at 2398 cm^{-1} which is tentatively assigned to the N-H band of the addition product of *N*-methyl-ε-caprolactam. The absorption band of CO of *N*-methyl-ε-caprolactam appears at 1645 cm^{-1}, which is shifted to the lower frequency than that of normal carbonyl compound, as shown in Fig. 11.

Discussion

ε-Caprolactam forms an addition compound with hydrogen chloride in carbon tetrachloride solution as follows

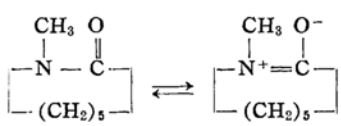


The ring opening reaction of ε-caprolactam in the presence of the ammonium cation[6] is presumed to be caused by the addition of the ammonium cation to the amide group.

The rate constant of hydrolysis of *N*-methyl-ε-caprolactam is about one twentieth of that of ε-caprolactam. The activation energy of hydrolysis of ε-caprolactam is calculated from the temperature dependence of the rate constants to be 20 kcal./mol., while that of *N*-methyl-ε-caprolactam 22 kcal./mol.

Since the molecular polarization of *N*-methyl-ε-caprolactam is almost constant with the increase of concentrations, it is expected that molecules do not associate at all. However, the absorption of CO in its infrared spectrum appears in much lower frequency than that of carbonyl compounds (about 1700 cm^{-1}). The dipole moment of *N*-methyl-ε-caprolactam is larger than that of ε-caprolactam.

From these results as stated above, it is expected that the amide linkage of *N*-methyl-ε-caprolactam has considerably ionic character due to resonance by the effect of methyl group as shown below and the stability of ring structure increases.



The rate constant of hydrolysis of ring-dimer is remarkably smaller than that of ε-caprolactam and that of ring-oligomers becomes faster as the ring becomes larger. It is ascertained[2,7] that the absorption of N-H of the *trans* or the *cis* amide appears in the 3370 to 3290 cm^{-1} or the 3240 to 3170 cm^{-1} regions in the infrared spectrum. The infrared spectrum of ring dimer, in the crystalline state, shows absorption maxima at 3279 and 3077 cm^{-1} and the configuration is expected to be not *cis*-[8] but *trans*- form. As the absorption band of CO of ring dimer appears in lower frequency than that of ε-caprolactam, ring-trimer or -tetramer, the low reactivity of ring dimer can be explained from the expectation that two amide groups are particularly favorable for the formation of two intramolecular hydrogen bonds and its structure is presumed to be as shown in Fig. 12. As amide groups lie too far apart to form the intramolecular hydrogen bond with the enlargement of the ring, the reactivity of ring oligomers becomes larger.

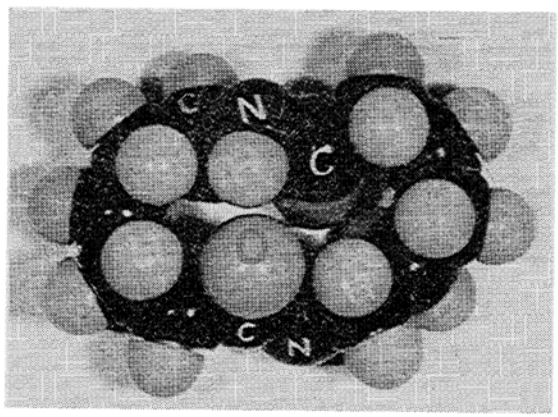


Fig. 12. The structure of ring dimer of ε-caprolactam.

Summary

The dipole moments, infrared spectra and rate constants of hydrolysis of ε-caprolactam derivatives have been determined in order to elucidate the difference in reactivity. The great stability of *N*-methyl-ε-caprolactam is expected, due to the increase of reasonance of amide linkage. Ring dimer of ε-caprolactam is stable for hydrolysis due to the strong intramolecular hydrogen bonds and the reactivity

6) H. Yumoto and N. Ogata, *Makromol. Chem.*, **25**, 71 (1958).
7) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1950).
8) P. H. Hermans, *Nature*, **177**, 126 (1956).

of ring oligomers of ε-caprolactam increases as the ring becomes larger.

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