

Kinetics of Reaction of C₂₁ Cycloaliphatic Dicarboxylic Acid and Ethylenediamine*

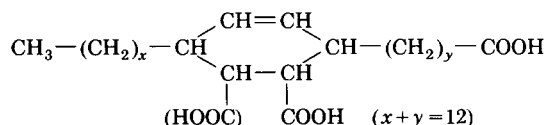
VIJAY KALE, P. VIJAYALAKSHMI, T. CHANDRASEKHARA RAO, R. SUBBARAO, and G. LAKSHMINARAYANA,[†] *Indian Institute of Chemical Technology (CSIR), Hyderabad-500 007, India,* and M. BHAGWANT RAO, *University College of Technology, Osmania University, Hyderabad-500 007, India*

Synopsis

Kinetic studies were carried out on the reaction between ethylenediamine and C₂₁ cycloaliphatic dicarboxylic acid, prepared from dehydrated castor oil fatty acids and acrylic acid, in melt phase. The reaction was performed at six different temperatures ranging from 210 to 260°C and followed by determining the acid value of the product. The polyamidation reaction was found to follow an overall third order kinetics with an activation energy of 15.5 kcal/g mol.

INTRODUCTION

Nonreactive polyamides derived from fatty acid-based dicarboxylic acids find extensive use in surface coatings, rotogravure and flexographic printing inks, and hot melt adhesives. Kinetic studies for preparation of polyamides such as nylon 6 and nylon 6,6 were reported.¹ Recent studies² on kinetics of polyamidation of C₃₆ dimeric fatty acids, in which both the carboxyl groups are primary, with ethylenediamine showed that the reaction followed overall second-order kinetics with an activation energy of 18.2 kcal/g mol up to 90% conversion and overall third-order kinetics with an activation energy of 16.4 kcal/g mol above 90% conversion. The present studies pertain to the kinetics of reaction of ethylenediamine with C₂₁ cycloaliphatic dicarboxylic acid, which has one primary and one secondary carboxyl groups, as shown below:



EXPERIMENTAL

Materials. C₂₁ cycloaliphatic dicarboxylic acid was prepared by Diels–Alder reaction of dehydrated castor oil (DCO) fatty acids and acrylic acid.³ The DCO fatty acids were obtained by hydrolysis of castor oil followed by

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[†]Address for correspondence: Dr. G. Lakshminarayana, Dy. Director & Head, Oils Division, Regional Research Laboratory, Hyderabad-500 007, India.

formation and decomposition of polyricinoleic acids and contained ca. 50% conjugated C_{18} dienoic and ca. 40% nonconjugated C_{18} dienoic acids.^{4,5} From the total reaction product of DCO fatty acids and acrylic acid, the unreacted monomer was removed by partition between aqueous methanol and petroleum ether (40–60°C)⁶ and the C_{21} dicarboxylic acid thus purified had a saponification value ca. 315 mg KOH/g. Ethylenediamine was laboratory reagent grade having purity of above 98% as determined by titration with standard acid. All other materials were reagent grade.

Method. The polyamidation reaction was carried out in a 1-L round bottom flask, equipped with a stirring assembly, nitrogen inlet tube, thermowell, dropping funnel, and a Dean–Stark arrangement attached to a water condenser. The flask was charged with a known weight (ca. 200 g) of the C_{21} dicarboxylic acid and heated using an isomantle to reach almost the required temperature. A molar equivalent quantity of ethylenediamine was added quickly within 2 min and the heating was regulated to get the desired temperature within 5–10 min. The water of reaction was swept off the system by bubbling nitrogen through the reacting melt at a sweep rate of 10 mL/min and was collected in the Dean–Stark arrangement. Removal of water from the system helped the reaction to go in the forward direction. The polyamidation reaction was carried out at six different temperatures ranging from 210 to 260°C. In this temperature range the reaction mass remained in molten state. Samples were taken out at intervals from the reaction medium and analyzed for acid value. Some samples were also analyzed for amine value. The acid and amine values were determined as per ASTM D-1980-67 and ASTM D-2074-62T, respectively, using a neutral solution (1:1, v/v) of ethanol and toluene for dissolving the samples.

RESULTS AND DISCUSSION

The polyamidation reaction was followed by determining the acid values of products obtained at six different temperatures ranging from 210 to 260°C. The amine values of some reaction products were determined and found to be almost equal to their acid values. This indicates that the reaction could be followed by the fall in either acid value or amine value of the product. The variation in acid value with reaction time is tabulated in Table I. The kinetics of the reaction was studied using integral method of analysis. Most of the polyamidation reactions reported in the literature⁷ were found to follow second-order kinetics up to about 90% conversion and thereafter the order of reaction was found to increase. In some cases of polyamidation above 90% conversion⁷ and in polyesterification,⁸ the reaction was reported to be carboxyl-catalyzed and followed third-order kinetics. In the present studies the fall in acid value with time was slow and nonlinear as is seen in Table I. This mode of fall in acid value might be due to the presence of one primary and one secondary carboxyl groups in the C_{21} dicarboxylic acid. The acid value versus time data did not fit an overall second-order kinetics. Hence it was assumed that the polyamidation reaction would follow a carboxyl-catalyzed overall third-order kinetics which is second order with respect to the carboxyl group

TABLE I
Variation of Acid Value with Reaction Time at Different Temperatures

Reaction time (h)	AV (mg KOH/g)	Reaction time (h)	AV (mg KOH/g)	Reaction time (h)	AV (mg KOH/g)
<u>210°C</u>		<u>220°C</u>		<u>230°C</u>	
0.33	77.0	0.33	72.5	0.33	63.6
0.67	58.8	0.67	52.2	0.67	46.2
1.00	53.1	1.00	43.0	1.00	38.4
2.00	37.8	1.33	38.1	2.00	27.0
3.00	30.7	2.33	30.0	3.00	24.2
4.00	26.1	3.33	25.7	4.00	20.5
5.00	23.4	4.33	22.1	5.00	18.3
6.00	21.8	5.33	19.7	6.00	15.9
		6.33	18.2		
<u>240°C</u>		<u>250°C</u>		<u>260°C</u>	
0.17	71.0	0.33	47.5	0.42	39.0
0.67	38.0	0.67	33.1	0.67	27.2
1.00	30.6	1.00	28.5	1.50	18.0
2.00	24.0	2.00	21.0	2.00	17.2
3.50	18.0	3.00	16.8	3.00	14.0
4.00	16.9	4.00	15.6	4.00	12.3
5.00	15.1	5.00	13.7		
6.00	13.5				

concentration and first order with respect to the amino group concentration.⁷ Since the reaction is homogeneous, the rate equation for this reaction can be written as

$$-\frac{dC_A}{dt} = KC_A^2 \cdot C_B \quad (1)$$

where C_A and C_B are the carboxyl and amino group concentrations present at any time t during the reaction.

Since molar equivalent amounts of the acid and amine are taken initially, the above equation after integration can be written as

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 2Kt \quad (2)$$

where C_{A0} and C_A = carboxyl group concentrations present initially and at time t (h), respectively, expressed as eq/10⁶ g polymer, K = third-order rate constant expressed as (eq/10⁶ g polymer)⁻² h⁻¹, and t = reaction time (h).

If $(AV)_0$ and AV are the acid values (mg KOH/g polymer) at time $t = 0$, i.e., the time at which both the reactants are brought into contact, and at time

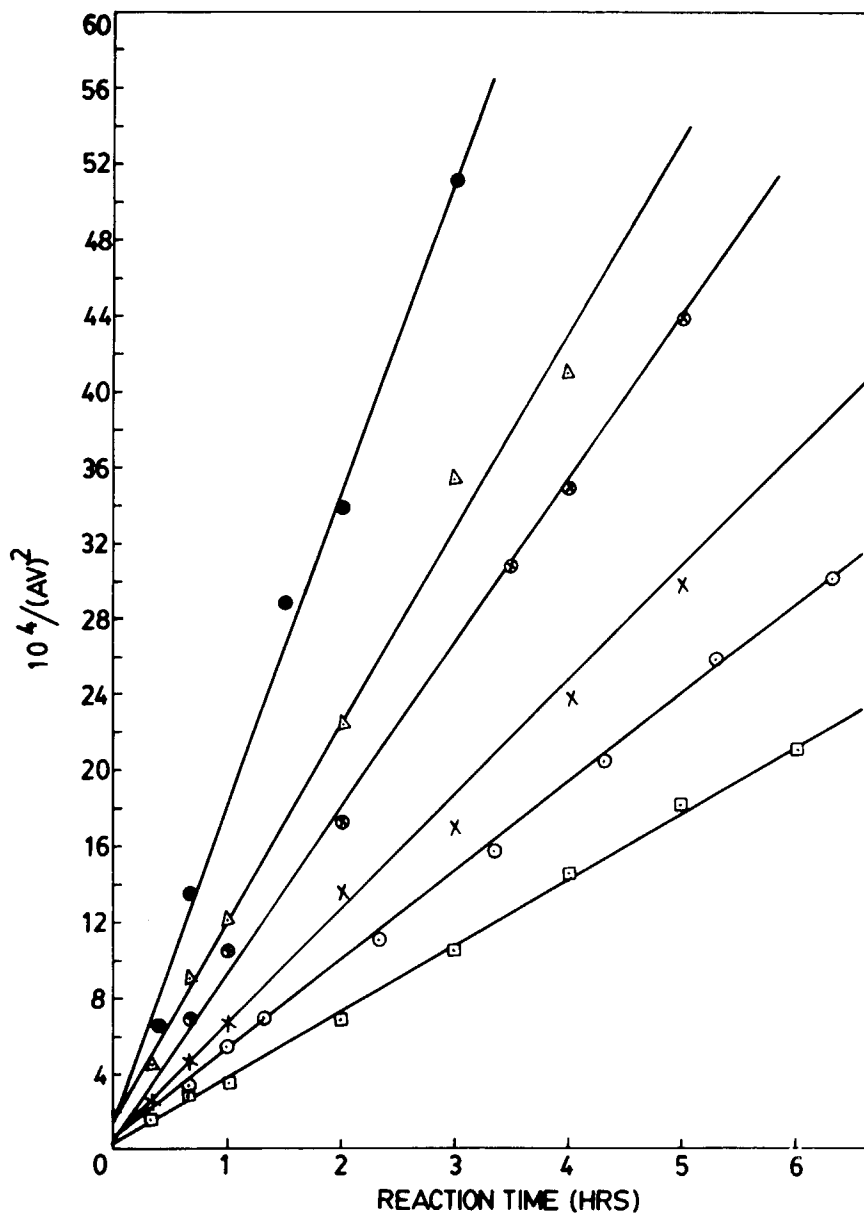


Fig. 1. Plot of $(a/AV)^2$ with time at different temperatures ($^{\circ}\text{C}$): (●) 260; (△) 250; (⊙) 240; (×) 230; (○) 220; (□) 210.

TABLE II
Third Order Reaction Rate Constants at Different Temperatures

Reaction temp (°C)	$K \times 10^7$ [(eq/10 ⁶ g polymer) ⁻² (h) ⁻¹]
210	5.538
220	7.283
230	9.725
240	13.489
250	16.375
260	26.799

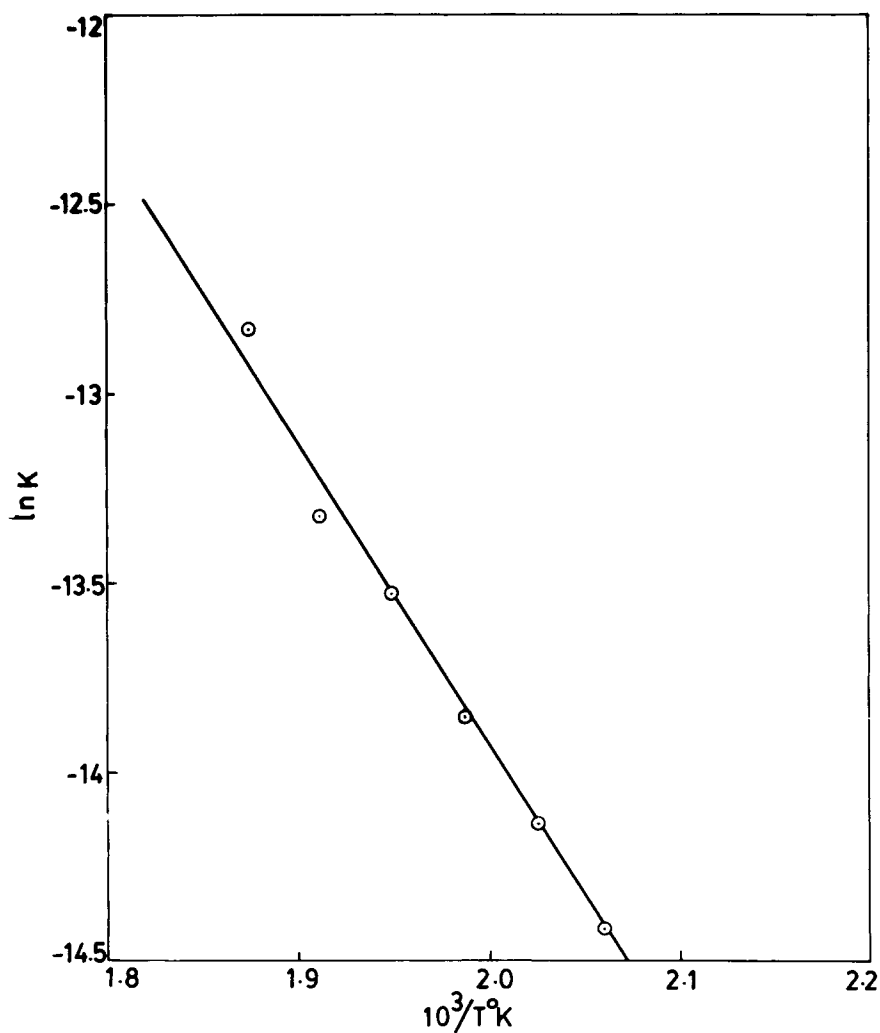


Fig. 2. Temperature dependency of reaction rate constant.

t (h), respectively, then C_{A0} and C_A can be expressed as

$$C_{A0} = \frac{10^6(AV)_0}{56,100}$$

and

$$C_A = \frac{10^6(AV)}{56,100}$$

Hence eq. (2) in terms of acid values can be written as

$$\frac{1}{(AV)^2} = \frac{2Kt}{(0.0561)^2} + \frac{1}{(AV)_0^2} \quad (3)$$

As per eq. (3) a plot of $1/(AV)^2$ vs. reaction time should be linear for a third-order kinetics. The plots of $1/(AV)^2$ vs. time in Figure 1 were found to be linear. This indicated that the reaction followed third-order kinetics at all the temperatures. The reaction rate constants calculated by the least square

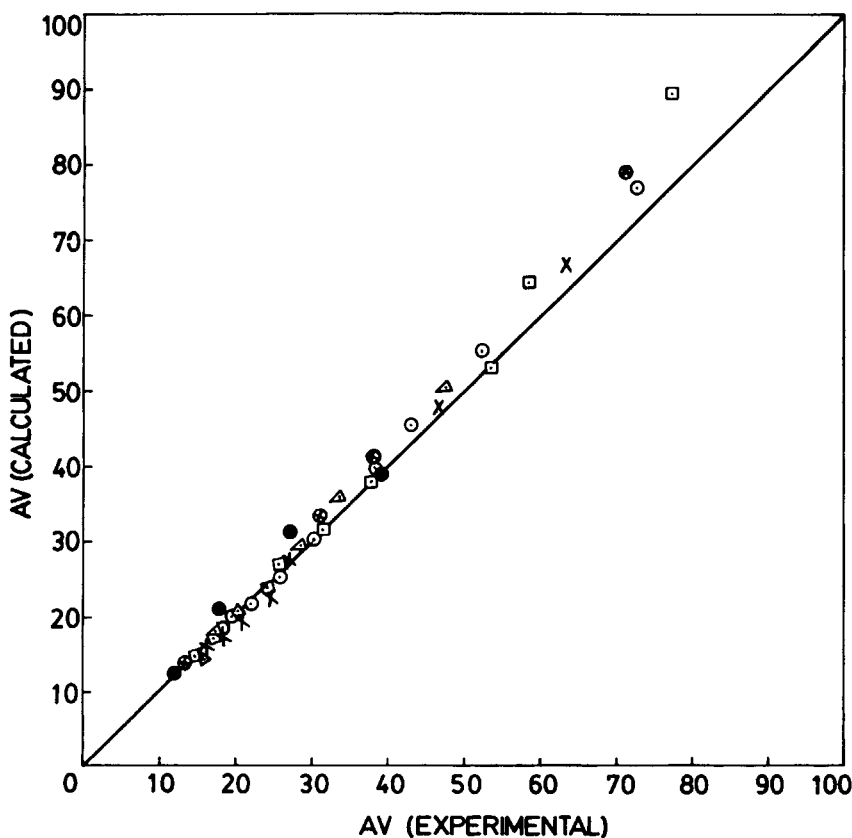


Fig. 3. Plot of AV (calculated) vs. AV (experimental) at different temperatures ($^{\circ}\text{C}$): (●) 260; (Δ) 250; (\odot) 240; (\times) 230; (\circ) 220; (\square) 210.

analysis of the data in Figure 1 are given in Table II. The reaction rate constants were found to fit the Arrhenius equation well as shown in Figure 2. The activation energy and frequency factor were calculated from the least square analysis of the data of Figure 2 and were found to be 15.5 kcal/g mol and $5.56 (\text{eq}/10^6 \text{ g polymers})^{-2} \text{ h}^{-1}$ respectively. Using these values of the activation energy and frequency factor, a generalized design equation for the reaction was deduced from eq. (3). The acid values calculated from this design equation were plotted against the experimental acid values at different temperatures as shown in Figure 3. The absolute percentage deviation between the experimental and calculated acid values was ca. 4%.

CONCLUSIONS

The melt phase polyamidation reaction between C₂₁ cycloaliphatic dicarboxylic acid and ethylenediamine is found to follow throughout an overall third-order kinetics and has an activation energy of 15.5 kcal/g mol. The sluggishness of the reaction may be due to the presence of one secondary carboxyl group in the C₂₁ dicarboxylic acid.

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