

Kinetics and Mechanism of Initial Steps of Synthesis of Polyetherols from Melamine and Ethylene Carbonate

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ABSTRACT: The kinetics of initial steps of formation of polyetherols in the reaction between melamine and ethylene carbonate in dimethylsulfoxide in presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as catalyst was studied. Based upon kinetic studies performed with various concentrations of melamine and catalyst, the rate law was formulated and a mechanism of the reaction was proposed. The

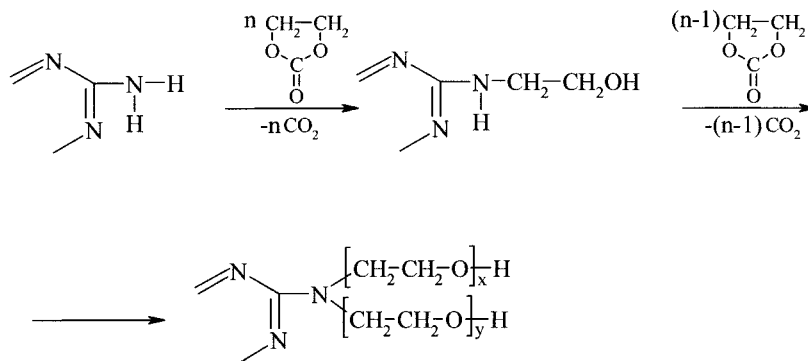
activation parameters ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger were obtained from the temperature dependence of kinetics. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 294–300, 2004

Key words: melamine; ethylene carbonate; kinetics; mechanism; oligomers; ring opening polymerization

INTRODUCTION

Polyetherols with a *s*-triazine ring are good components for obtaining polyurethane foams of outstanding thermal resistance.¹ They can be synthesized in the reaction of melamine or its *N*-hydroxyethyl derivatives with oxiranes, such as ethylene oxide or propylene oxide.^{2–5} These synthetic routes were disadvantageous due to the lack of convenient solvents for melamine, flammability and toxicity of oxiranes, and multistep reaction. The

mechanistic and kinetic studies were performed for those reactions in detail.^{6,7} Recently we have proposed a simple, one-step method of synthesis of polyetherols with a *s*-triazine ring based on a straightforward reaction between melamine with an excess of ethylene or propylene carbonates, thus avoiding these disadvantages.^{8,9} The scheme of the synthetic route is shown below (the relevant fragment of the melamine molecule is drawn in the scheme):



where $x + y = n$

The reaction was catalyzed by potassium hydroxide and carbonate or 1,4-diaza-bicyclo[2.2.2]octane (DABCO).

Although the alkylene carbonates were found to be useful reagents in industry,^{10,11} the kinetics and mechanism of reaction between melamine and alkylene carbonates was not studied until now. Here we have attempted to describe the initial steps of the reaction be-

tween melamine and ethylene carbonate, i.e., the reaction formation of a nitrogen-carbon bond in which amine nitrogen from melamine (Mel) and methylene carbon from ethylene carbonate (EC) are involved. The mechanism of reaction is proposed based upon rate law and activation parameters of the reaction.

EXPERIMENTAL

Kinetic measurements

The kinetic runs were performed by addition of variable amounts of EC and DABCO into a preheated solution of 6.3 g Mel (0.05 mol, pure, Merck, recryst-

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tallized from water before use) in 55 g of dimethylsulfoxide (DMSO, pure, Avocado, dried over molecular sieves A-4). After the addition of the reagents at constant temperatures: 140, 150, 160, and 170°C, the progress of reaction was monitored by analytical determination of unreacted EC.

The kinetics was studied for

1. various molal concentrations of functional groups of Mel for [Mel] = 0.909, 1.212, and 1.818 mol/kg of solvent, at constant [EC] = 0.909 mol/kg and [DABCO] = 0.81 $\cdot 10^{-2}$ mol/kg;
2. various concentrations of DABCO at constant [Mel] = 0.909 mol/kg and [EC] = 1.818 mol/kg. The concentrations of DABCO was varied within 0.81×10^{-2} and 12.98×10^{-2} mol/kg and were 0.81×10^{-2} ; 1.62×10^{-2} ; 3.24×10^{-2} ; 6.49×10^{-2} ; and 12.98×10^{-2} mol/kg;
3. various EC concentrations at constant [Mel] = 0.909 mol/kg and [DABCO] = 3.24×10^{-2} mol/kg. The concentration of EC was varied: 0.909; 1.818; 2.727; 3.636; 4.545; and 5.454 mol/kg of solvent.

Parameters of activation were obtained from kinetic runs with initial concentrations of [Mel] = 0.909 mol/kg, [EC] = 1.818 mol/kg, and [DABCO] = $3.24 \cdot 10^{-2}$ mol/kg at temperatures 140–170°C by monitoring the reaction for 3–17 h.

Determination of unreacted EC

The 0.1–0.2 g aliquot of reaction mixture was placed in a beaker and then 10 cm³ water and three drops of 0.2% alcoholic solution of tymolphthaleine were added. The solution was neutralized with 0.1M HClaq if necessary. Then 2.5 cm³ of 0.15M Ba(OH)₂ was added and the beaker was firmly stopped and vigorously shaken for 10 min. The excess of barium hydroxide was titrated with 0.1M HCl. The blank was prepared in the same way. The percentage of unreacted ethylene carbonate $p_{\%EC}$ was determined from the formula:

$$p_{\%EC} = \frac{0.51 \times (V_0 - V_1)}{m} \quad (2)$$

where V_0 , V_1 are the volume of HCl solution used for blank and for a sample, respectively, [cm³] and m is the mass of sample, [g].

In calculations the molal concentration was used due to variable mass and density of reaction mixture.

The energy of activation was obtained from the thermal dependence of rate constant according to eq. (3):

$$\Delta G^\# = RT \left(23.764 - \ln \frac{k}{T} \right) \quad (3)$$

where k is the rate constant and $k = k_{3/2}$ taken from eq. (10) (*vide infra*), and T is the temperature [K].

TABLE I
Rate Constants for the Reaction Between Mel and EC at 150°C ($c_{0AH} = 5.454$ mol/kg; $c_{0cat} = 3.2467 \cdot 10^{-2}$ mol/kg)

Entry	c_{0BC} [mol/kg]	$c_{0AH}:c_{0BC}$	$k_{3/2} \cdot 10^5$ [mol ^{-1/2} · kg ^{1/2} · s ⁻¹]
1	0.4432	12.3:1	74.1 ± 3.7
2	0.6920	7.89:1	55.9 ± 7.9
3	0.9149	5.96:1	43.4 ± 6.8
4	1.8192	2.99:1	26.9 ± 1.9
5	2.8069	1.94:1	15.5 ± 0.9
6	3.5667	1.52:1	10.2 ± 0.4
7	4.5455	1.20:1	9.36 ± 0.46
8	5.4959	0.99:1	7.71 ± 0.54

The $\Delta G^\# = f(T)$ plot was approximated with straight line, from which $\Delta H^\#$ and $\Delta S^\#$ were obtained according to the relationship [eq. (4)]:

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \quad (4)$$

¹H-NMR spectroscopy

The ¹H-NMR spectra were recorded with a Bruker AMX 300 MHz instrument in DMSO-*d*₆ at 353 K.

RESULTS AND DISCUSSION

Despite the fact that polyetherols can be obtained in the reaction of Mel with neat EC, the kinetic studies were performed in the DMSO solvent to achieve the homogeneous solution conditions. It was demonstrated before that Mel did not dissolve completely in EC, when less than 9 moles of EC was used.^{8,9} In those conditions the initial step of the reaction between Mel and EC is rather heterogeneous. Moreover, the initial products of the reactions, i.e., hydroxyethyl derivatives of Mel are very soluble in EC and react faster than Mel itself, resulting in faster consumption of EC in consecutive reactions. The DMSO was chosen as solvent for kinetic measurements due to its high boiling point. Kinetic runs were conducted in the presence of DABCO, which was demonstrated to be a good catalyst for these reactions.^{8,9}

It has been found that kinetics of the reaction in presence of a molar excess of reactive groups of Mel (AH) in relation to number of moles of EC (BC) followed the rate law [eq. (5)]:

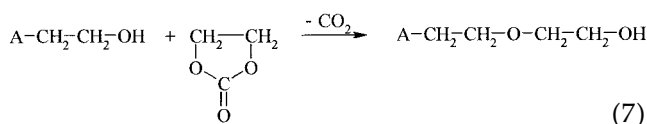
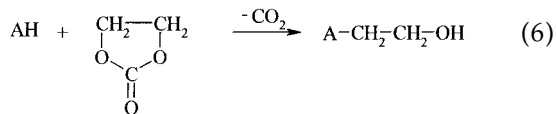
$$V = -\frac{dc_{BC}}{dt} = k_{3/2} \times c_{BC}^{3/2} \quad (5)$$

where c_{BC} is the current concentration of EC.

The order of reaction for EC (3/2) is preserved even at equimolar amounts of EC in relation to Mel (Table I, entry 8). The changes of relative concentrations of

EC: $b = c_{BC}/c_{0BC}$ (where c_{0BC} is the initial concentration of EC) in time for various concentrations of the reactive groups of Mel are illustrated at Figure 1.

The reaction of Mel with EC is composed of two steps: (1) the reaction of reactive groups of Mel with EC [eq. (6)] and (2) reactions of hydroxyethyl derivatives of Mel with EC [eq. (7)]:



To avoid the consecutive reaction [eq. (7)], the six-molar excess of AH was used in kinetic studies. In separate control experiments we have found that, under the conditions used here, the DABCO does not influence the kinetics of the reaction between 2-hydroxyethyl groups with EC.

Thus, assuming that $c_{AH} = \text{const}$, the relationship [eq. (8)] holds:

$$k_{3/2} = k'_{3/2} \times C_{AH}^m \quad (8)$$

Using this equation the values of m and $k'_{3/2}$ were estimated (Fig. 2).

Introducing the calculated values the initial kinetic, eq. (5) was modified into eq. (9):

$$V = k'_{3/2} \times c_{AH}^{1/2} \times c_{BC}^{3/2} \quad (9)$$

The value of $k'_{3/2}$ in experimental eq. (9) should be the same as k'_r calculated from eq. (10), in which no constant c_{AH} was assumed:

$$V = k'_r \times (c_{0AH} - x)^{1/2} \times (c_{0BC} - x)^{3/2} \quad (10)$$

where c_{0AH} , c_{0BC} are the initial concentrations of reactive groups of Mel and EC (mol/kg) and x is the change of concentration of EC due to reaction with AH, which is equal to the change of concentration of AH in the absence of consecutive reactions.

As can be seen from data collected in Table II, the rate constants calculated from eqs. (9) and (10) are almost the same so long as $c_{0AH} > 3 c_{0BC}$. When $c_{0AH} < 3 c_{0BC}$, the comparison of $k'_{3/2}$ becomes impossible due to the involvement of consecutive reactions.

The influence of the catalyst concentration was studied for the system in which a threefold excess of AH related to EC was present (Fig. 3). There is a simple relationship between k'_r calculated from eq. (10) and the concentration of the catalyst:

$$k'_r = k''_{3/2} \times c_K^z \quad (11)$$

where c_K is concentration of catalyst [mol/kg], $k_{3/2}'$ is the rate constant for the 1 mol/kg solution of catalyst, from which $z = 1/2$ (Fig. 3).

Thus, a general kinetic equation for the reaction between Mel and EC was derived [eq. (12)]:

$$V = k''_{3/2} \cdot c_K^{1/2} \cdot c_{AH}^{1/2} \cdot c_{BC}^{3/2} \quad (12)$$

where $c_{AH} = 6 \times c_{MEL}$.

Based upon this experimentally obtained equation, the mechanism of reaction can be postulated as being composed of the following steps, which are represented by elementary reactions [eqs. (13–18)] and summarized afterward (*vide infra*).

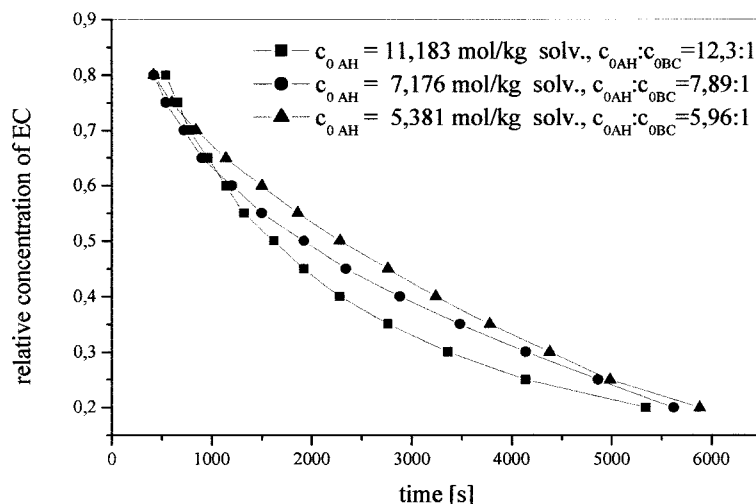


Figure 1 Changes of relative concentration of EC in the course of reaction for various concentration of Mel.

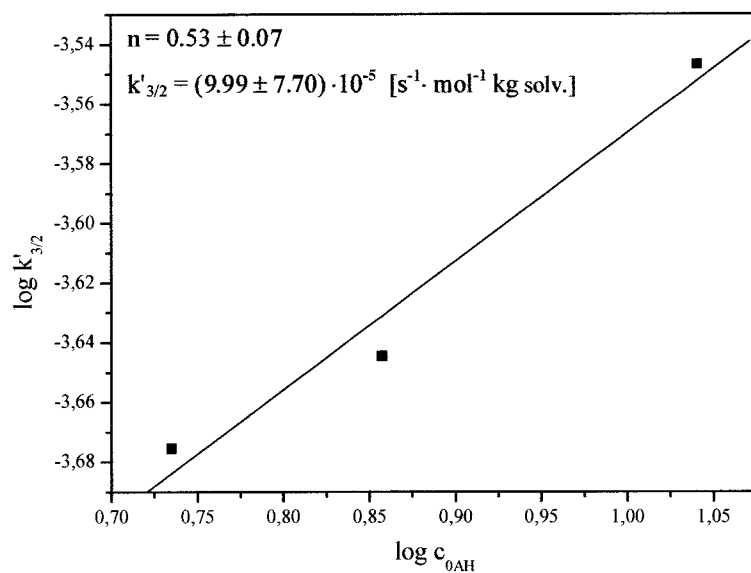


Figure 2 The plot $\log k'_{3/2}$ vs $\log c_{0AH}$ for the reaction of Mel with EC in presence of DABCO ($c_{0BC} = 0.9091$ mol/kg, $c_{cat} = 8.168 \cdot 10^{-3}$ mol/kg).

TABLE II
Comparison of Rate Constants for the Reaction Between Mel and EC Obtained from Kinetic Eqs (9) and (10) ($c_{0AH} = 5.454$ mol/kg; $c_{0cat} = 3.24 \cdot 10^{-2}$ mol/kg)

Molar ratio of reactive groups of Mel into EC $c_{0AH} : c_{0BC}$	$k_{3/2} \cdot 10^4$ [$\text{mol}^{-1/2} \cdot \text{kg}^{1/2} \cdot \text{s}^{-1}$]	$k'_{3/2} = (k_{3/2} c_{0AH}^{-1/2}) \cdot 10^4$ [$\text{mol}^{-1} \cdot \text{kg}^1 \cdot \text{s}^{-1}$]	$k_r \cdot 10^4$ [$\text{mol}^{-1} \cdot \text{kg}^1 \cdot \text{s}^{-1}$]
24:1	11.60	4.97	5.00
12:1	7.41	2.22	2.22
8:1	6.87	2.44	2.41
6:1	4.09	1.75	1.79
3:1	2.69	1.15	1.19
2:1	1.55	0.65	0.73
1.5:1	1.02	0.43	0.51
1.2:1	0.93	0.40	0.47
1:1	0.71	0.30	0.23

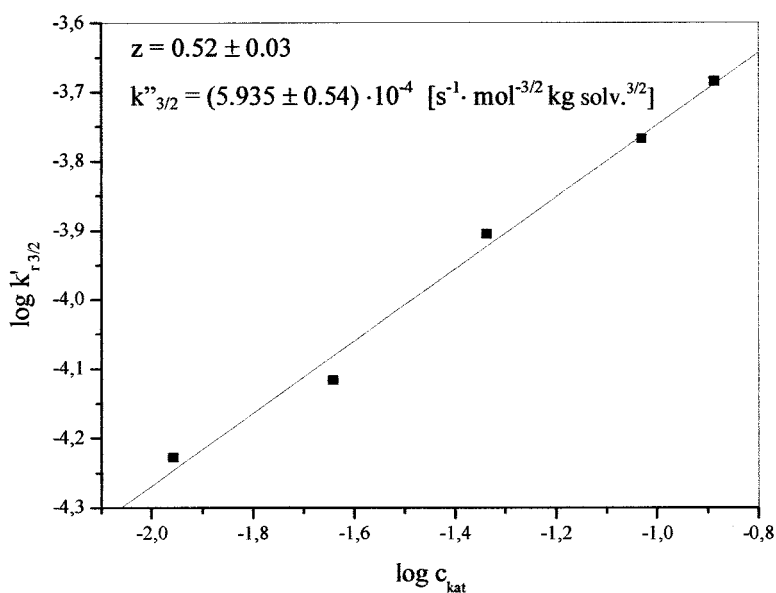
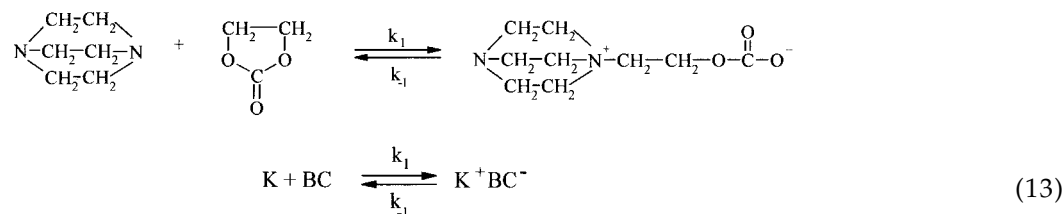
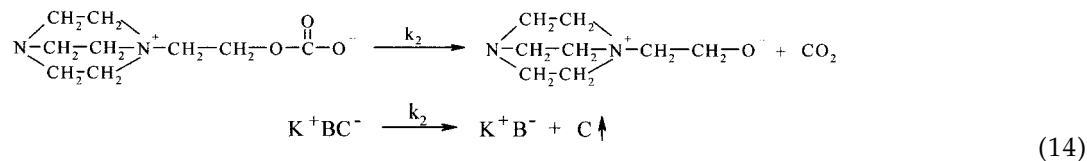


Figure 3 The plot $\log k'_{r,3/2}$ vs $\log c_{cat}$ for the reaction of Mel with EC in presence of variable concentration of DABCO ($c_{0AH} = 5.4546$ mol/kg, $c_{0BC} = 1.8181$ mol/kg).

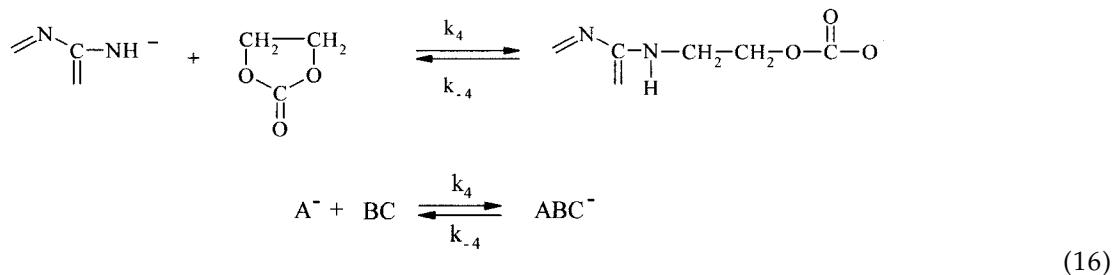
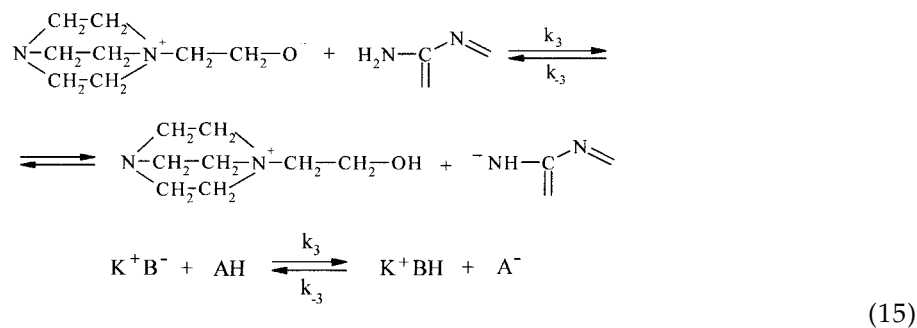
I.



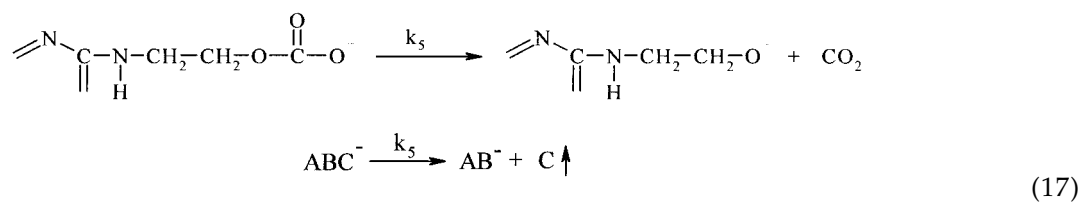
II.



III.



V.



VI.

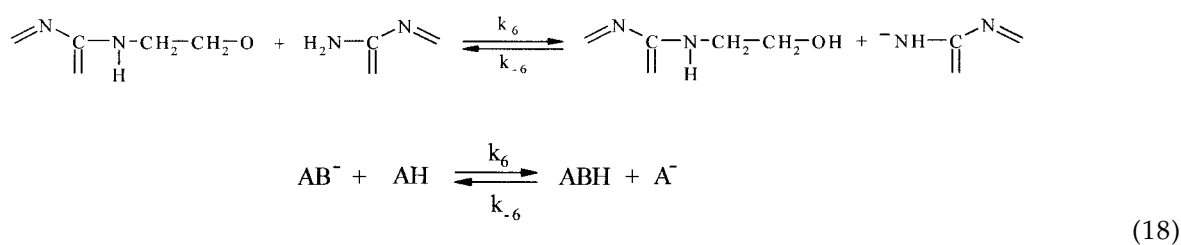


TABLE III
Temperature Dependence of Rate Constants for the
Reaction Between Mel and EC ($c_{0\text{AH}} = 5.4546 \text{ mol/kg}$;
 $c_{0\text{BC}} = 1.8182 \text{ mol/kg}$; $c_{0\text{cat}} = 8.116 \cdot 10^{-3} \text{ mol/kg}$)

T [K]	$k_{3/2}'' \cdot 10^4$ [$\text{s}^{-1} \cdot \text{mol}^{-3/2} \text{kg}^{3/2}$]
413	2.69 ± 0.25
423	5.51 ± 0.10
433	14.64 ± 1.66
443	25.74 ± 2.91

According to the proposed mechanism, the elementary steps can be formulated as

1. the attack of the catalyst on EC with formation of a precatalyst K^+, BC^- [eq. (13)].
2. Conversion of precatalyst KBC into catalyst K^+, B^- with release of CO_2 [eq. (14)].
3. Proton transfer from primary or secondary amine group of Mel into KB [eq. (15)].
4. The attack of anion of melamine on next molecule of EC with formation of carbonate ABC^- [eq. (16)].
5. Cleavage of carbonate into alcoholate AB^- [eq. (17)].
6. Proton transfer from next amine group into alcoholate with recovery of anion of melamine (A^-) [eq. (18)].

Assuming that the limiting step is eq. (16), the general kinetic equation becomes

$$V_g = k_4 \times c_{\text{A}^-} \times c_{\text{BC}} \quad (19)$$

The concentration of A^- can be obtained from the equilibrium constant for reaction (15):

$$K_3 = \frac{c_{\text{K}^+\text{BH}^-} \times c_{\text{A}^-}}{c_{\text{K}^+\text{B}^-} \times c_{\text{AH}}} \quad (20)$$

Because $c_{\text{K}^+\text{BH}^-} = c_{\text{A}^-}$, the eq. (20) simplifies into eq. (21):

$$K_3 = \frac{c_{\text{A}^-}^2}{c_{\text{K}^+\text{B}^-} \times c_{\text{AH}}} \quad (21)$$

from which

$$c_{\text{A}^-} = K_3^{1/2} \times c_{\text{K}^+\text{B}^-}^{1/2} \times c_{\text{AH}}^{1/2} \quad (22)$$

The concentration of K^+, B^- is equal to that of K^+, BC^- because reaction (14) is irreversible. Thus

$$c_{\text{A}^-} = K_3^{1/2} \times c_{\text{K}^+\text{BC}^-}^{1/2} \times c_{\text{AH}}^{1/2} \quad (23)$$

In which the concentration of K^+, BC^- can be calculated from the equilibrium constant of reaction (13):

$$K_1 = \frac{c_{\text{K}^+\text{BC}^-}}{c_{\text{K}} \times c_{\text{BC}}} \quad (24)$$

$$c_{\text{K}^+\text{BC}^-} = K_1 \times c_{\text{K}} \times c_{\text{BC}} \quad (25)$$

Introducing eq. (25) into eq. (23), the concentration of A^- can be obtained from eq. (26):

$$c_{\text{A}^-} = K_3^{1/2} \times K_1^{1/2} \times c_{\text{K}}^{1/2} \times c_{\text{BC}}^{1/2} \times c_{\text{AH}}^{1/2} \quad (26)$$

Eventually, after introducing this expression into eq. (19), the general rate law is obtained [eq. (27)]:

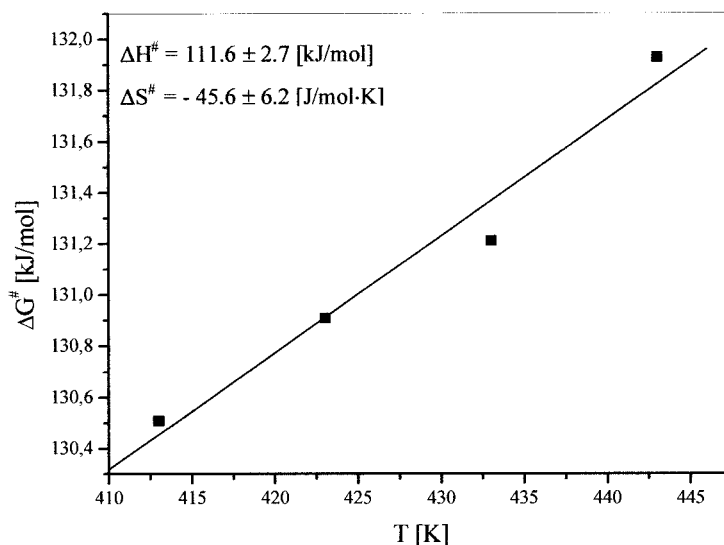
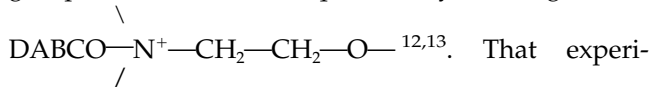


Figure 4, Temperature dependence of energy of activation for the reaction between Mel and EC.

$$V_g = k_4 \times K_3^{1/2} \times K_1^{1/2} \times c_k^{1/2} \times c_{BC}^{1/2} \times c_{AH}^{1/2} \times c_{BC} = k_4'' \times c_k^{1/2} \times c_{BC}^{3/2} \times c_{AH}^{1/2} \quad (27)$$

The derived equation is in accordance with that obtained experimentally. This suggests that the assumed mechanism is correct. We have examined the solutions containing DABCO and EC at molar ratio 1 : 5 by $^1\text{H-NMR}$ spectroscopy. A triplet (or doublet of doublets) centered at 3.1 ppm in the spectrum taken at 80°C was attributed to the protons of a methylene group attached to quarternary nitrogen of



That experiment provided evidence for formation of the postulated active form of the catalyst (K^+B^-). On the other hand the progress of reaction between EC and Mel in the absence (and in the presence) of DABCO could be followed by the disappearance of 6.0 ppm resonance from H_2N (Mel) with the simultaneous growing of a new peak at 6.3 ppm, attributed to NHCH_2OH (6.3 ppm) as it was previously described.⁸

The activation parameters for the reaction of Mel with EC in presence of DABCO were obtained from the temperature dependence of $k_{3/2}''$ within a range of 410–450 K (Table III, Fig. 4). The large value of enthalpy of activation (111.6 kJ/mol) for the studied system (Mel + EC) in comparison with that for the analogous system with ethylene oxide (EO, $\Delta H_{\text{EO}}^\#$

= 72.2 kJ/mol⁸) probably results from higher thermodynamic stability of the five-membered ring of alkylene carbonate in comparison of the three-membered ring of oxirane. On the other hand, a more positive entropy of activation (-45.6 J/mol K) in comparison with that for the reaction with oxirane (-103 J/mol K^8) is due to the fact that the slowest step in the former reaction is a decarboxylation of precatalyst. That reaction as well as formation of linear etherol chains from cyclic molecules of ethylene carbonate lead to an increase of entropy.

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