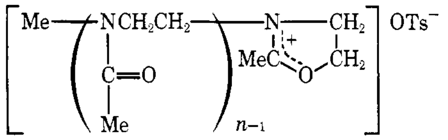
Isomerization Polymerization of 2-Oxazoline. IV. Kinetic Study of 2-Methyl-2-oxazoline Polymerization

Takeo Saegusa,* Hiroharu Ikeda, and Hiroyasu Fujii

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

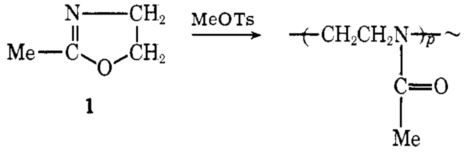
Received February 25, 1972

ABSTRACT: A kinetic study of the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) initiated by methyl tosylate (MeOTs) was performed on the basis of the determination of the instantaneous concentrations of MeOTs, MeOXZ, and the propagating species of oxazolinium salt by means of nmr spectroscopy. The rate was expressed by the equation $-d[M]/dt = k_i[\mathrm{MeOTs}][M] + k_{p1}[P_1^*][M] + k_{pn}[M]\Sigma_{n=2}[P_n^*]$. In this equation, k_i, k_{p1}, and k_{pn} are the rate constants for the initiation, the first propagation step, and the propagation steps after the first one, respectively. $[P_1^*]$ and $[P_n^*]$ ($n \geqq 2$) are the instantaneous concentrations of the propagating species of two types having $n = 1$ and $n \geqq 2$, respectively, in $[\mathrm{Me(N(COMe)CH_2CH_2)}_{n-1}$-



$\mathrm{MeOXZ^+}]\mathrm{OTs^-}$. It is to be noticed that the rate constants of k_{p1} and k_{pn} ($n \geqq 2$) are different from each other. The values of rate constants were determined at 31, 40, and 50°, from which the activation parameters of the respective elementary reactions were obtained.

The present study deals with the kinetics of the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) (**1**) initiated by methyl tosylate (MeOTs) in deuterated acetonitrile (CD_3CN). As to the kinetics of the polymerization of the 2-substituted 2-oxazolines, two studies have already been made by Tomalia, *et al.*,[1] and by Kagiya, *et al.*[2] The present study is characterized by the direct determinations of the instantaneous concentrations of MeOTs (initiator), MeOXZ (monomer), and the propagating species of oxazolinium salt by means of nmr spectroscopy. The polymerization of this study was found to proceed through a living mechanism, and the rate constants of three elementary reactions, (i) initiation, (ii) the first propagation, and (iii) the propagation after the first one, were successfully obtained.



1

Experimental Section

Reagents. 2-Methyl-2-oxazoline (MeOXZ). MeOXZ was prepared and purified as previously reported.[3] Methyl tosylate (MeOTs) was a commercial reagent which was purified by distillation under nitrogen. Trideuterioacetonitrile (CD_3CN), the polymerization solvent, was a commercial reagent which was dried by molecular sieves 4A (Union Carbide) and then distilled under nitrogen.

***N*-Methyl-2-methyl-2-oxazolinium Tosylate (2).** This oxazolinium salt was similarly prepared as reported in the preceding paper[3] by the reaction of MeOXZ with MeOTs in ether solvent.

Polymerization and Nmr Measurement. The whole operation was carried out under nitrogen. MeOTs, 0.184 g (0.988 mmol), was added at the polymerization temperature to a stirred solution of 4.94 mmol (0.421 g) of MeOXZ in 0.86 ml of CD_3CN containing 0.04 ml of tetramethylsilane. Then, a small portion of the reaction mixture was transferred into an nmr tube and the polymerization was continued in the tube at constant temperature. The instantaneous concentrations [M] (monomer), [MeOTs] (initiator), and [P*] (propagating species), were determined from nmr spectra recorded at several reaction times on a Varian HA-100 nmr spectrometer. The experimental error of the nmr spectroscopy is below ±10%.

Polymer Molecular Weight. Polymer obtained in the parent batch was subjected to a molecular weight determination by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in $CHCl_3$ at 37°. The polymer sample had been purified by reprecipitation using a combination of CH_3CN (solvent) and ether (precipitant).

Results and Discussion

Polymerization of MeOXZ Initiated by MeOTs. Nmr Spectroscopy. Figure 1 shows the nmr spectrum of the MeOXZ polymerization system initiated by MeOTs in CD_3CN at 40°, which was taken at a reaction time of 0.5 hr. The assignments of the peaks are well accommodated by the scheme of reactions 1–3. The peaks at τ 2.60 and 2.82 were assigned respectively to the aromatic protons (H_2–C_6H_2S) of the unreacted and the reacted CH_3OTs, whose areas were conveniently utilized to determine the extent of the initiation reaction of eq 1. The monomer concentration was determined on the basis of the peaks of the three different methyl groups, *i.e.*, the 2-methyl group of the unreacted MeOXZ at τ 8.10, the *N*-acetyl group of the product polymer at τ 8.02, and the 2-methyl group of the oxazolinium ring at τ 7.71. All three of these peaks are derived from the initial MeOXZ monomer, and, consequently, the instantaneous monomer concentration was calculated from its fraction among three peaks and the initial monomer concentration. As to the peak of the oxazolinium methyl group at τ 7.71, the half peak area was adopted because the peak suffers from the overlap with the methyl group of its counteranion, $CH_3C_6H_4SO_3^-$, having the same concentration. The combined concentration of two types of propagating species, P_1^* and P_n^* ($n \geqq 2$),

---

(1) A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A-1*, 4, 2253 (1966).

(2) T. Kagiya and T. Matzuda, presented at 19th Polymer Symposium Kyoto, 1970; Abstracts, p 155.

(3) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 3, in press.

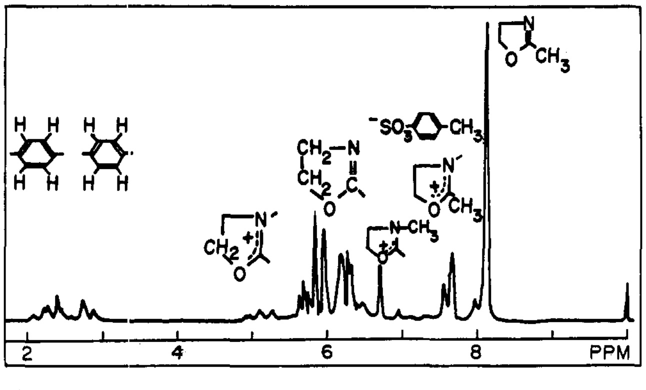
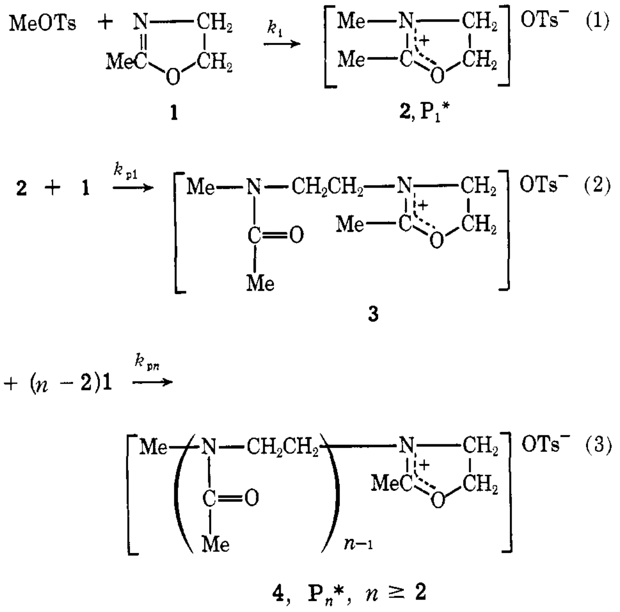


Figure 1. Nmr spectrum of the MeOXZ polymerization system initiated by MeOTs in CD_3CN (after 0.5 hr at 40°).

is given by the peak at τ 5.20 ($O-CH_2$). On the other hand, $[P_1^*]$ and $[P_n^*]$ ($n \geqq 2$) are determined separately by independent means, *i.e.*, $[P_1^*]$ is given by the peak at τ 6.80 (N^+-CH_3) due to **2**, and $[P_n^*]$ ($n \geqq 2$) is estimated on the assumption of living polymerization mechanism from the peak area at τ 7.03 which is assigned to the terminal *N*-methyl group (CH_3-N) of the propagating polymer molecule. The living polymerization mechanism was established by an experiment described below.



1

2, P_1^*

3

4, P_n^*, $n \geq 2$

Figure 2 shows the nmr spectrum of the reaction system of the polymerization with a feed ratio of MeOXZ/MeOTs = 5. The reaction was done at 40° for a sufficiently long time of 30 hr until the monomer was polymerized completely. According to the peak assignment given in the preceding part, the amounts of the polymer repeating units and the propagating species were determined, from which the degree of polymerization was calculated as 5. This value by nmr coincided well with the feed ratio of monomer/initiator = 5. In addition, the actual molecular weight of the polymer sample prepared in the parent batch under the same conditions was found by vapor pressure osmometry to be 678, which was not much different from the calculated value of 612 for the degree of polymerization of 5. These findings are taken to support the view that every molecule of MeOTs initiates the polymerization and the all propagating species continue to grow. Also, the assignment of nmr spectrum has become valid.

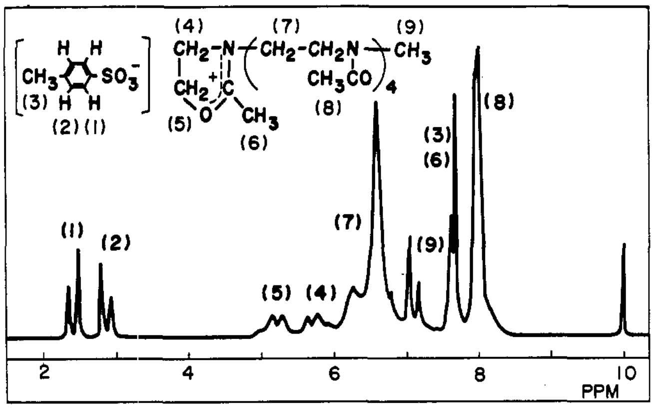


Figure 2. Nmr spectrum of the MeOXZ polymerization system initiated by MeOTs in CD_3CN (after 30 hr at 40°).

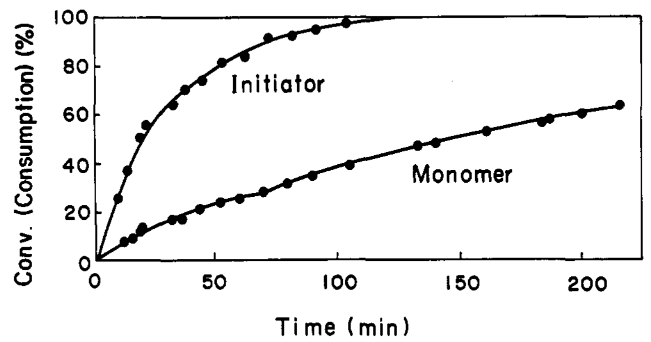


Figure 3. Time–conversion curves of the MeOXZ polymerization initiated by MeOTs in CD_3CN at 40°; [MeOXZ] 3.33 *M*, [MeOTs] 0.667 *M*.

Kinetics. Figure 3 shows the time–conversion curves for the MeOTs initiator and MeOXZ monomer. MeOTs has been consumed in an early period of polymerization. In the conversion curve of MeOXZ, a refractive point was observed in a region where MeOTs was almost consumed. Figure 4 gives the time–total [P*] relationship. It is observed that [P*] increases with the consumption of MeOTs in the initial stages of reaction, and then it remains almost constant after all MeOTs has been consumed. The stoichiometry between the total [P*] at the later stage of polymerization and the feed concentration of MeOTs is satisfactory.

Now, the following kinetic equation is given on the basis of the scheme of eq 1–3.

$$-\frac{d[M]}{dt} = k_i[\text{MeOTs}][M] + k_{p1}[P_1^*][M] + k_{pn}[M]\sum_{n=2}[P_n^*] \quad (4)$$

In order to carry out the kinetic analysis, an expedient procedure was tentatively adopted, in which k_{p1} was equal to k_{pn}. Then, the rate equation becomes

$$-\frac{d[M]}{dt} = k_i[\text{MeOTs}][M] + k_p[P^*][M] \quad (5)$$

where $k_p = k_i = k_{pn}$ and $[P^*] = [P_1^*] + \Sigma_{n=2}[P_n^*]$. Since [P*] was found by nmr to be equal to the amount of the conversion of MeOTs

$$[P^*] = [\text{MeOTs}]_0 - [\text{MeOTs}] \quad (6)$$

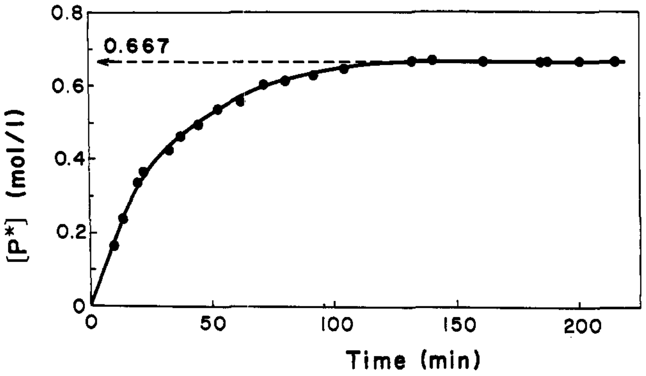


Figure 4. Time–total [P*] curve of the MeOXZ polymerization initiated by MeOTs in CD_3CN at 40°; [MeOXZ] 3.33 *M*, [MeOTs] 0.667 *M*.

where $[\text{MeOTs}]_0$ is the initial concentration of MeOTs. Therefore

$$-\frac{d[M]}{dt} = (k_i - k_p)[\text{MeOTs}][M] + k_p[\text{MeOTs}]_0[M] \quad (7)$$

Integration of eq 7 gives

$$\ln [M]_0/[M] = (k_i - k_p)\int_0^t [\text{MeOTs}]dt + k_p[\text{MeOTs}]_0 t \quad (8)$$

Therefore

$$\frac{\ln [M]_0/[M]}{\int_0^t [\text{MeOTs}]dt} = (k_i - k_p) + k_p\frac{[\text{MeOTs}]_0 t}{\int_0^t [\text{MeOTs}]dt} \quad (9)$$

The integrated value of [MeOTs] in eq 9 was given by graphical integration on the [MeOTs]–time curve in Figure 3. Figure 5 represents a plot of eq 9 in the polymerization at 40°, which consists of two straight lines, A and B, having different slopes and intercepts. The plot of Figure 5 is taken to suggest that k_{p1} is not equal to k_{pn}. However, the straight line A was conveniently utilized to calculate k_i and k_{p1}, because the nmr analysis showed that $[P_n^*]$ ($n \geqq 2$) was quite small in an early period of polymerization, $[P_n^*]$ ($n \geqq 2$) = 0. Then, k_p in eq 12 is k_{p1} in the period of the straight line A. Thus k_{p1} was obtained from the slope of A and k_i was calculated from the intercept; $k_{p1} = 0.77 \times 10^{-4}$ and $k_i = 1.8 \times 10^{-4}$ l./(mol sec) at 40°. On the other hand, in the later stages of polymerization, $[P_1^*]$ was found to be very small, *i.e.*, $[P_1^*] = 0$ and k_p in eq 12 is regarded as k_{pn} in the period corresponding to the straight line B. From the slope of B, k_{pn} was calculated as 1.17×10^{-4} l./(mol sec). The rate of initiation was determined also by the rate of consumption of MeOTs using the peaks at τ 2.60 and 2.82, because the stoichiometry between the concentrations of reacted MeOTs and the total propagating species has been established. Thus

$$-d[\text{MeOTs}]/dt = k_i[\text{MeOTs}][M]$$

The rate constant k_i was determined from the slope of the linear plot of the integrated equation (Figure 6).

$$\ln\frac{[\text{MeOTs}]_0}{[\text{MeOTs}]} = k_i\int_0^t [M]dt + C \quad (10)$$

The k_i value at 40° thus obtained was 1.8×10^{-4} l./(mol sec), which agreed well with that value obtained in the preceding paragraph.

Kinetics of Polymerization Initiated by Oxazolinium Salt (P_1^*). An oxazolinium salt of **2** was prepared from MeOXZ and MeOTs according to a previous procedure[3] which was used as the polymerization initiator. The polymerization commences directly from the first propagation step of k_{p1}. Figure 7 shows the courses of the decrease of $[P_1^*]$ (curve 1) and the increases of $[P_n^*]$ ($n \geqq 2$) (curve 2) as well as the conversion percent of MeOXZ (curve 3). Here, the changes of the concentrations of three species, MeOXZ, $[P_1^*]$, and $[P_n^*]$ were followed by the nmr spectrum. A stoichiometric relation is clearly seen between the amounts of the $[P_1^*]$ consumption and the $[P_n^*]$ production.

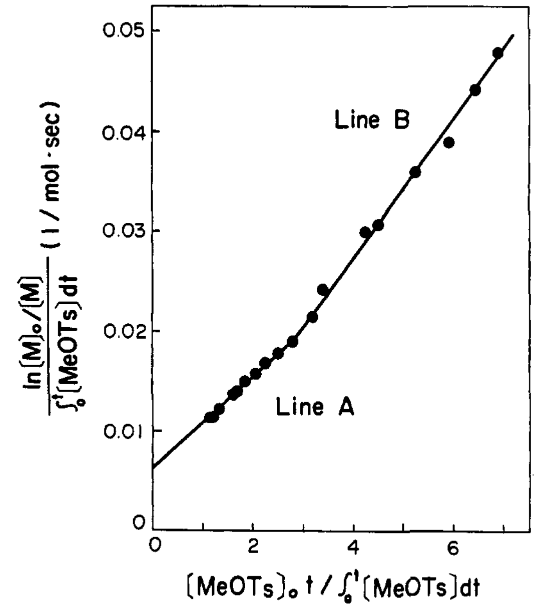


Figure 5. Plot of eq 9 in the MeOXZ polymerization by MeOTs at 40°.

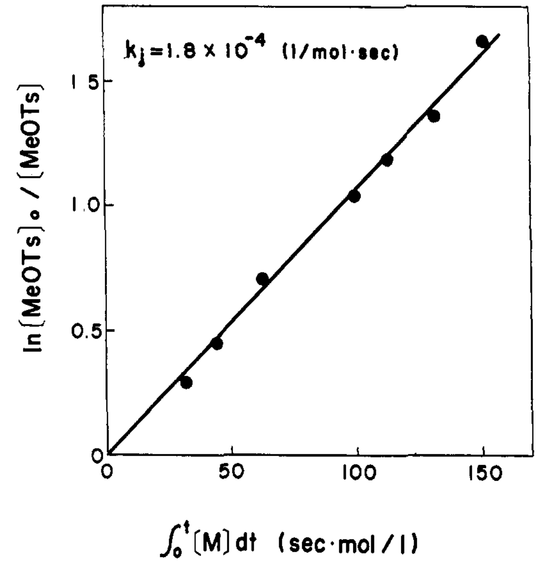


Figure 6. Linear plot of the integrated eq 10 in the MeOXZ polymerization by MeOTs at 40°.

The rate of the polymerization initiated by **2** is expressed by

$$-\frac{d[M]}{dt} = k_{p1}[P_1^*][M] + k_{pn}[M]\sum_{n=2}[P_n^*] \quad (11)$$

Since $\Sigma_{n=2}[P_n^*] = [P_1^*]_0 - [P_1^*]$ was actually observed (Figure 7), eq 11 becomes

$$-\frac{d[M]}{dt} = (k_{p1} - k_{pn})[P_1^*][M] + k_{pn}[P_1^*]_0[M] \quad (12)$$

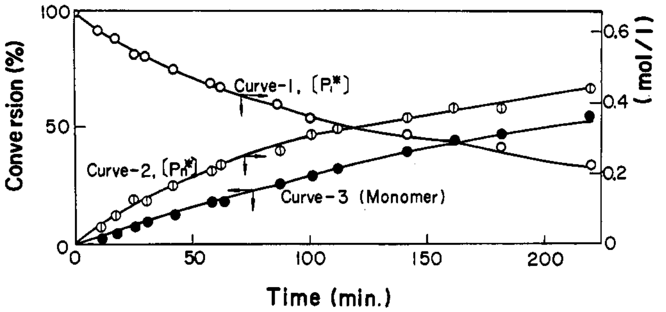


Figure 7. Course of the MeOXZ polymerization initiated by *N*-methyl-2-methyl-2-oxozolinium salt **2** in CD_3CN at 40°; $[P_1^*]$, concentration of oxazolinium salt (curve 1); $[P_n^*]$ ($n \geq 2$), concentration of propagating species (curve 2).

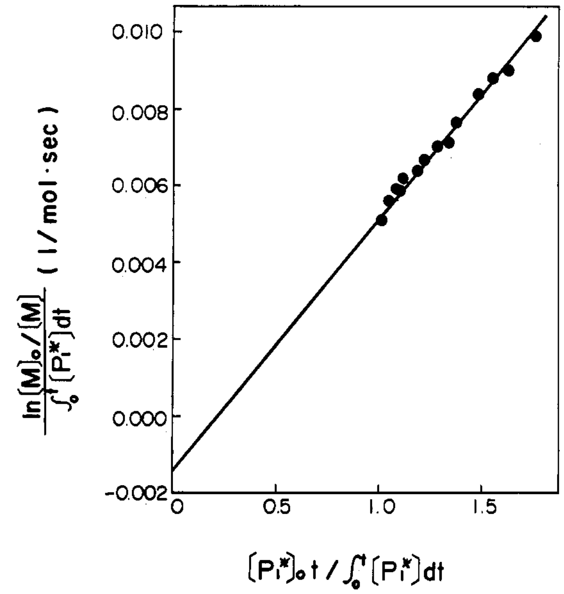


Figure 8. Plot of eq 13 in the MeOXZ polymerization by MeOXZ–MeOTs salt at 40°.

The integration form is

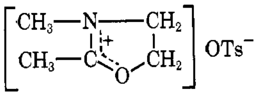
$$\frac{\ln [M]_0/[M]}{\int_0^t [P_1^*]dt} = (k_{p1} - k_{pn}) + k_{pn} \frac{[P_1^*]_0 t}{\int_0^t [P_1^*]dt} \qquad (13)$$

TABLE I
RATE CONSTANTS[a] AND ACTIVATION PARAMETERS OF THE MeOXZ POLYMERIZATION INITIATED BY MeOTs IN CD_3CN[b]

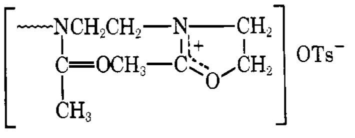
Temp, °C	$k_i \times 10^4$	$k_{p1} \times 10^4$	$k_{pn} \times 10^4$
31	0.90	0.40	0.49
40	1.82	0.77	1.17
50	4.0	1.58	3.1
E, kcal/mol	14.4	13.7	19.1
A, l./(mol sec)	1.7×10^6	5.7×10^5	1.9×10^9

[a] Rate constants are expressed in l./(mol sec). [b] Polymerization conditions, [MeOXZ] 3.33 *M*, [MeOTs] 0.667 *M*.

In the plot of eq 13, the integrated value of $[P_1^*]$ was obtained by graphical integration of curve 1 of Figure 7. Figure 8 indicates the linear plot of eq 13, which the slope is k_{pn} and the intercept is $(k_{p1} - k_{pn})$. The values of the rate constants at 40° were $k_{p1} = 0.86 \times 10^{-4}$ and $k_{pn} = 1.09 \times 10^{-4}$ l./(mol sec). The agreement is remarkable between the k_{p1} values given in the two polymerization runs initiated by MeOTs and by **2**. In addition, the k_{pn} value is very close to the value obtained from the straight line B in Figure 5. The difference between the rate constants of the first propagation step and the subsequent steps is an important finding. The difference of reactivity between **2** and **4** is not incomprehensible from the view that the *N*-acetyl carbonyl group of the penultimate group has an interaction with the carbonium center of the cyclic oxazolinium at the growing end.



2



4

Activation Parameters. In addition to the preceding experiments at 40°, the polymerization with the MeOTs initiator was done at 31 and 50°. The rate constants k_i, k_{p1}, and k_{pn} at three temperatures are summarized in Table I. The Arrhenius plots of these three rate constants were all linear, from which the activation parameters of respective elementary reactions were obtained (Table I).