Macromolecules

Volume 6, Number 5 September–October 1973

Studies on the Ring-Opening Polymerization of Cyclic Ethers. Kinetics of Initiation Reaction by Triethyloxonium Tetrafluoroborate

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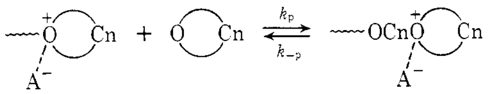
Received March 12, 1973

ABSTRACT: This paper describes a kinetic study on the oxonium-exchange reaction between triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) and a series of cyclic ethers. The purpose of the study is to elucidate the mechanism of the initiation reaction of the cationic ring-opening polymerization of cyclic ethers. Cyclic ethers employed in this study were tetrahydrofuran, tetrahydropyran, and oxepane. The rates at various temperatures were determined by means of nmr technique, which gave the initiation rate constants (k_i) as well as the activation parameters. The k_i values at 35° in CH_2Cl_2 were as follows: tetrahydrofuran, 1.50×10^{-3}; tetrahydropyran, 1.34×10^{-3}; and oxepane, 1.08×10^{-3} l./(mol sec), respectively. The order of the magnitude of k_i was tetrahydrofuran > tetrahydropyran > oxepane, although the differences are not considerable. The k_i value can be taken as a measure of the nucleophilicity of monomer toward the common oxonium ion. The order of the nucleophilicities expressed by k_i values was discussed in comparison with the monomer basicity. The kinetics of the initiation reaction also was compared with that of the propagation reaction, which is a bimolecular reaction between the cyclic oxonium of propagating species and the cyclic ether monomer. The k_i value of tetrahydrofuran is much smaller than its k_p. The big difference has been attributed to the difference of reactivity between the acyclic oxonium ($Et_3O^+BF_4^-$) and cyclic oxonium.

The cationic ring-opening polymerization of cyclic ethers has been known to proceed *via* an SN2 reaction between the cyclic oxonium ion of propagating species (electrophile) and monomer (nucleophile)

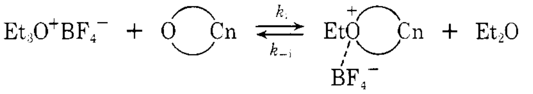


(1)

By means of our "phenoxyl end-capping method,"[1] the propagation rate constants, k_p, have been determined on several monomers having different ring sizes and structures.[2-5] Based on the k_p values thus obtained, the kinetic reactivities of polymerization of cyclic ethers have been quantitatively discussed.[6]

As to the initiation reaction, however, very few kinetic studies have been available, so far.[7] When an oxonium salt is used as initiator the initiation reaction proceeds also through an SN2 process, where the monomer attacks the α-carbon atom of the oxonium ion. This mechanism resembles the propagation in which the monomer attacks the α-carbon atom of the propagating cyclic oxonium ion. For the analysis of the propagation reaction, the reactivities of the cyclic oxonium ion (electrophile) and the monomer (nucleophile) are to be estimated separately.

In the present study the kinetics were made on the reactions between triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) and tetrahydrofuran, tetrahydropyran, and oxepane in CH_2Cl_2 solvent (eq 2). These reactions correspond to the initiation of the cyclic ether polymerizations.



(2)

$n = 4, 5, 6$

Also, the results can be taken as a measure of the relative nucleophilicities of cyclic ethers in the propagation.

Experimental Section

Materials. Monomers and CH_2Cl_2 were purified as previously reported.[2-4] Their purities were shown to be higher than 99.9% by glpc analyses. $Et_3O^+BF_4^-$ was synthesized and purified by Meerwein's procedure.[8] The purification of $CHCl_3$ was made according to a well-known method.[9]

Determination of the Reaction Rate. The whole operation was carried out under nitrogen. Into a mixture (5 ml) of CH_2Cl_2 (solvent) and a small amount of $CHCl_3$ (internal standard), 4.78 mmol of $Et_3O^+BF_4^-$ and 6.27 mmol of monomer were dissolved at the reaction temperature, which resulted in the concentrations of 0.800 mol/l. for the former and 1.05 mol/l. for the latter. Then, a small portion of the reaction mixture was transfered into an nmr tube and the reaction was continued in the tube at a con-

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(3) T. Saegusa, Y. Hashimoto, and S. Matsumoto, *Macromolecules,* 4, 1 (1971).

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(7) Y. Yamashita, S. Kozawa, M. Hirota, K. Chiba, H. Matsui, A. Hirao, M. Kodama, and K. Ito, *Makromol. Chem.,* 142, 171 (1971).

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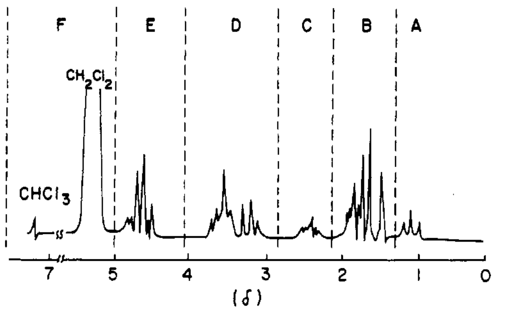


Figure 1. Nmr spectrum of the $Et_3O^+BF_4^-$-tetrahydrofuran reaction system after 20 min at 35° in CH_2Cl_2 using $CHCl_3$ as internal standard.

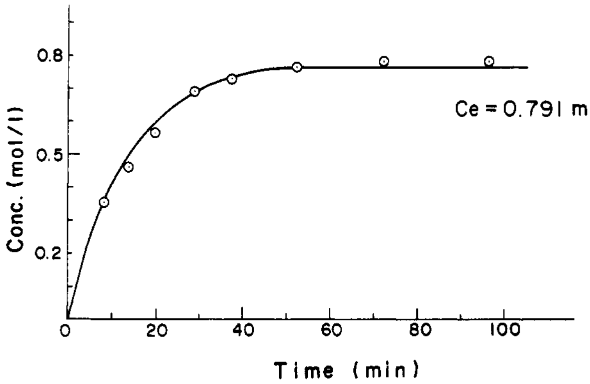


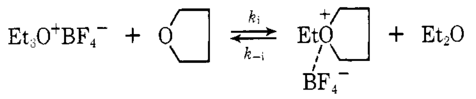
Figure 2. Time-conversion curve of the $Et_3O^+BF_4^-$-tetrahydrofuran reaction system at 35° in CH_2Cl_2.

stant temperature. The instantaneous concentrations of the products, [C] (cyclic trialkyloxonium ion and diethyl ether) were determined from nmr spectra recorded at several reaction times on a Hitachi R-20B nmr spectrometer. The experimental error of the nmr spectroscopy was within ±2%.

Results and Discussion

Determination of the Reaction Rates. Figure 1 illustrates the nmr spectrum of the reaction system of $Et_3O^+BF_4^-$ with tetrahydrofuran in CH_2Cl_2 at the reaction time of 20 min at 35°. The spectrum is conveniently divided into six regions (A ~ F). Yamashita *et al.*[7] also reported almost the same nmr spectrum as that of Figure 1. The assignments of signals in each region are given in Table I.

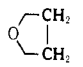
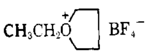
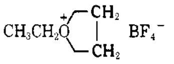
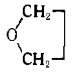
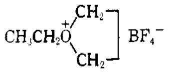
The following relationships (eq 3) are given for the concentration of each component


(3)

at time 0	$[C_0]$	$[M_0]$	-	-
at time *t*	$[C_0] - [C]$	$[M_0] - [C]$	$[C]$	$[C]$

where $[C_0]$ and $[M_0]$ represent the initial concentrations of $Et_3O^+BF_4^-$ and tetrahydrofuran, respectively, [C] represents the concentrations of the products, cyclic oxonium $[EtO^+(CH_2)_4](BF_4^-)$ and diethyl ether, and k_i and k_{-i} denote the rate constants of the initiation and the reverse reaction, respectively. The stoichiometry of eq 3 was shown valid for the integral value of each region on the basis of that of the internal standard of $CHCl_3$ as given in the third column of Table I. Furthermore, from the proton signal at the β position of the cyclic oxonium (C region) and the methyl signal of diethyl ether (A region), the [C] *vs.* time relationship was successfully constructed as given in Figure 2. Both values of [C] obtained from the C and A regions were in satisfactory agreement with each other.

Table I
Assignment of Signals of Figure 1 and Integral Values

Region	Assignment	Integral Value
A	$(CH_3CH_2)_2O$	6[C]
B		$4([M_0] - [C]) + 3[C] + 9([C_0] - [C]) = 4[M_0] + 9[C_0] - 10[C]$
		
	$(CH_3CH_2)_3O^+BF_4^-$	
C		4[C]
D	$(CH_3CH_2)_2O$	$4[C] + 4([M_0] - [C]) = 4[M_0]$
		
E	$(CH_3CH_2)_3O^+BF_4^-$	$6([C_0] - [C]) + 6[C] = 6[C_0]$
		
F	$CHCl_3$	$[S_0]$

Now, it is possible to analyze these results on the basis of the typical second-order kinetics as described below. The rate of the product formation of eq 3 is given as follows

$$dc/dt = k_i([C_0] - [C])([M_0] - [C]) - k_{-i}[C^2] \quad (4)$$

and the equilibrium constant of eq 3, $1/K$, is expressed by

$$\frac{1}{K} = \frac{k_i}{k_{-i}} = \frac{[C_e^2]}{([C_0] - [C_e])([M_0] - [C_e])} \quad (5)$$

where $[C_e]$ is the concentration of the cyclic oxonium at equilibrium which is determined from Figure 2. Then, eq 4 is transformed by using eq 5 into

$$dc/dt = k_i\{(1 - K)[C^2] - ([M_0] + [C_0])[C] + [M_0][C_0]\} \quad (6)$$

Using α and β, which are the two roots of the equation $(1 - K)x^2 - ([M_0] + [C_0])x + [M_0][C_0] = 0$, eq 6 becomes

$$dc/dt = k_i(1 - K)(\alpha - [C])(\beta - [C]) \quad (7)$$

where

$$\alpha = \frac{1}{2(1 - K)}\left\{[M_0] + [C_0] + \sqrt{([M_0] + [C_0])^2 - 4([M_0][C_0])(1 - K)}\right\}$$

$$\beta = \frac{1}{2(1 - K)}\left\{[M_0] + [C_0] - \sqrt{([M_0] + [C_0])^2 - 4([M_0][C_0])(1 - K)}\right\} \quad (8)$$

Then, eq 7 can be easily integrated from t_1 to t_2 and $[C_1]$ to $[C_2]$, respectively, to give

$$k_i = \frac{2.303}{(1 - K)(\alpha - \beta)(t_2 - t_1)} \times \log\left[\frac{(\beta - [C_1])(\alpha - [C_2])}{(\alpha - [C_1])(\beta - [C_2])}\right] \quad (9)$$

The $1/K$ value could be determined from Figure 2 ac-

Table II
Initiation Rate Constants at Various Temperatures[a]

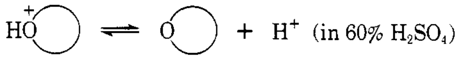
	$k_i \times 10^4$ (l./(mol sec))			
	35°	25°	16°	2.5°
Tetrahydrofuran	15.$_0$		3.9$_6$[b]	0.61$_0$
Tetrahydropyran	13.$_4$	5.3$_8$	2.1$_9$	
Oxepane	10.$_8$	5.1$_0$	1.8$_3$	

[a] $[M]_0$ = 1.05 mol/l., $[Et_3O^+BF_4^-]_0$ = 0.800 mol/l. in CH_2Cl_2. [b] k_i at 17°.

Table III
Comparison of Initiation with Propagation

	Initiation[a]		Propagation[b]	
	$k_i \times 10^3$ (l./(mol sec)) at 35°	$1/K$	$k_p \times 10^3$ (l./(mol sec)) at 0°	Monomer Basicity[c] pK_a
Oxetane			140[d]	
Tetrahydrofuran	1.5$_0$	36	4.1[e]	−2.08
Tetrahydropyran	1.3$_4$	23		−2.79
Oxepane	1.0$_8$	26	0.015[f]	−2.02

[a] This work. [b] With BF_3 initiator in CH_2Cl_2. [c] See ref 11. The pK_a values were obtained from the reaction



[d] From ref 3. [e] From ref 2. [f] From ref 4.

cording to eq 5. Then, α and β of eq 8 were calculated. In two experiments with tetrahydrofuran, $1/K$ values were 38 and 34; then, the mean value of 36 was adopted. Finally k_i was successfully obtained according to eq 9, $k_i = 1.50 \times 10^{-3}$ l./(mol sec) at 35°.

In a similar way kinetic analyses were successfully performed with tetrahydropyran and oxepane. The results are shown in Table II.

In the case of tetrahydrofuran, the kinetics were carried out at a tetrahydrofuran monomer concentration of 1.05 mol/l., which was smaller than the equilibrium concentration of monomer (1.7 mol/l. at 0° and 4.0 mol/l. at 35°).[10] In fact no polymerization was observed during kinetic runs under the reaction conditions. As to oxepane, the equilibrium monomer concentration was determined by us,[5] as 0.06 mol/l. at 10° and 0.08 mol/l. at 30°. The oxepane concentration of the present kinetic condition was higher than these equilibrium concentrations. However, the propagation of oxepane has been found to be so slow[4] that the initiation took place almost exclusively before going into propagation. Thus, the occurrence of the oxepane propagation was actually not observed during kinetic runs. In the case of tetrahydropyran, no polymerization took place.

As seen in Tables II and III, the k_i values are in the order of tetrahydrofuran > tetrahydropyran > oxepane, although they lie in a narrow range. This order is not the same as that of the basic strengths of these cyclic ethers (pK_a). Furthermore, the order of the equilibrium constants ($1/K$) is not in correlation with that of pK_a values. The difference between the reactivity order of the cyclic ethers toward oxonium and the order of basic strength may be attributed to the difference of the electrophiles, Et_3O^+ and H_3O^+,[11] respectively. Table III shows also the following facts, *i.e.*, in the tetrahydrofuran polymerization, the propagation is much faster than the initiation, but in the oxepane polymerization the propagation is slower than the initiation.

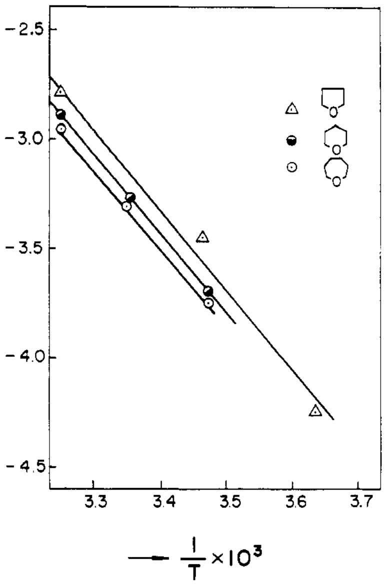


Figure 3. Arrehnius plots of initiation rate constants of three monomers.

Table IV
Kinetic and Thermodynamic Data of Four Monomers

	Initiation[a]		Propagation[b]		Ring Strain[c]
	ΔH_i^* (kcal/mol)	ΔS_i^* (eu)	ΔH_p^* (kcal/mol)	ΔS_p^* (eu)	ΔH_s (kcal/mol)
Oxetane			14[d]	−12	25.1
Tetrahydrofuran	16.$_4$	−15.$_9$	12[e]	−26	5.2
Tetrahydropyran	16.$_4$	−16.$_3$			−0.7
Oxepane	16.$_2$	−17.$_3$	18[f]	−16	5.2

[a] This work. [b] All kinetic data were obtained with BF_3 initiator in CH_2Cl_2. [c] From ref 12. [d] From ref 3. [e] From ref 13. [f] From ref 4.

Activation Parameters of Initiation. The Arrhenius plots of the k_i values of three cyclic ethers are shown in Figure 3, from which the activation parameters have been calculated (Table IV). The activation enthalpies of initiation of three monomers (ΔH_i^*) are almost the same values of about 16 kcal/mol. Hence the small difference of k_i values is not due to the activation enthalpy but it is due to the activation entropy, ΔS_i^*.

Comparison between Initiation and Propagation. The rate constants (k_i) of the oxonium exchange reaction (eq 2) of three cyclic ethers with a common electrophile of $Et_3O^+BF_4^-$ are taken to represent their relative nucleophilicities, which have been shown to vary to a small extent. On the other hand, the rate constant of the propagation of the cyclic ether polymerization, which is an S_N2 reaction between cyclic oxonium (electrophile) and monomer (nucleophile) (eq 1), varies very much depending on the ring size of monomer (Table III). The propagation rate may be controlled by the inherent ring-opening reactivity

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(10) E. A. Ofstead, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 6, 674 (1965).

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of cyclic oxonium and the nucleophilicity of monomer. The entropy factor is also important. The results of the present study have shown that the nucleophilicity of monomer which varies very little depending on the monomer ring size is not a determining factor in the big difference of the propagation rate constant between the tetrahydrofuran and oxepane polymerizations.

In the consideration of the mechanism of the propagation, the values of activation parameters of the propagation in the polymerizations of four-, five-, and seven-membered cyclic ethers (Table IV) are quite informative. It is seen that the rate is controlled by complicated combinations of the activation enthalpy and entropy. It is of interest to note that the activation enthalpy of the propagation of a more strained monomer of oxetane (as is seen from ΔH_s[12] in Table IV) is higher than that of a less strained monomer of tetrahydrofuran. Also, the propagation rate constant of oxepane, which is more strained than tetrahydrofuran,[5] is smaller than that of tetrahydrofuran. Thus, the strain in the cyclic ether monomer is not related to the activation enthalpy of propagation. The results of the kinetic analysis in the polymerizations of a series of cyclic ethers have clearly shown that an element of the activation entropy is very important for governing the rate of propagation.[6] The activation entropy may possibly be determined by the solvation (initial state)-desolvation (transition state) phenomena as well as the spatial orientations of the electrophile (the propagating species of cyclic oxonium structure) and the nucleophile (the monomer) in the transition state.[13]

Very recently, it has been reported[14] that the tetrahydrofuran polymerization proceeds *via* two species, *e.g.*, the free ion and the ion pair. However, the contribution of the free ion to the overall k_p is not so large that the over all k_p obtained previously by us seems to permit the above discussion of reactivity. Studies on the reactivity of cyclic oxonium species are necessary for the full understanding of the propagation of the cationic polymerization of cyclic ethers.

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Free-Radical Polymerization of 1-Ferrocenyl-1,3-butadiene and 1-Phenyl-1,3-butadiene. Reactivity Ratios and *Q* and *e* Values

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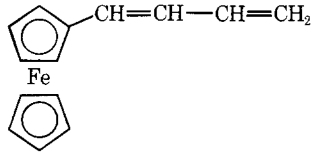
Received March 29, 1973

ABSTRACT: The monomers 1-ferrocenyl-1,3-butadiene (1) and 1-phenyl-1,3-butadiene (2) have been synthesized and their characteristics in homopolymerization reactions and in copolymerization reactions with styrene have been investigated. Glpc and elemental analysis data have been used to calculate polymerization rates, reactivity ratios, and *Q* and *e* values for monomers 1 and 2. For the styrene-butadienylferrocene system, $r_1 = 0.76 \pm 0.01$, $r_2 = 2.47 \pm 0.01$, ($Q = 1.56$, $e = -0.80$); for the styrene-butadienylbenzene system, $r_1 = 0.71 \pm 0.01$, $r_2 = 1.20 \pm 0.01$ ($Q = 1.49$, $e = -0.79$). Low molecular weight polymers were obtained in all cases. For the styrene-butadienylferrocene system, $\bar{M}_n$ ranged from 1300 to 1950; for the styrene-butadienylbenzene system, $\bar{M}_n$ ranged from 1700 to 3800.

Many polymers that contain the ferrocene nucleus have been prepared and studied in recent years and these have been reviewed recently.[1] These polymers are of interest because of their potential electrical and magnetic properties, their catalytic activity, and their redox properties, to mention only a few. In many polymer applications, a controlled amount of cross-linking of polymer chains is desirable after the polymer forming reaction has been accomplished. The monomers, 1-ferrocenyl-1,3-butadiene (**1**) and 1-phenyl-1,3-butadiene (**2**), thus have the potential of undergoing vinyl addition copolymerization, and subsequently reacting with suitable cross-linking agents to form a cross-linked polymer by thermal treatment. The determination of reactivity ratios of monomer pairs in copolymerization reactions is of considerable importance, since the chemical composition of a copolymer depends mainly upon the relative reactivities of the two monomers toward the two intermediate radicals. Studies of the relative reactivities of vinyl monomers have been numerous, but similar information on conjugated diene monomers is less extensive. The purpose of this investigation was to homopolymerize **1** and **2**, and to copolymerize them with each other as well as with styrene, so that some comparison of their relative reactivity in free-radical-initiated polymerizations could be made.



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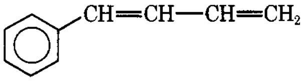

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Results and Discussion

Homopolymerization. The free-radical homopolymerization of **1** in degassed benzene solution at 70° with azodiisobutyronitrile as an initiator provided poly(butadienylferrocene) in 37% conversion (Figure 1). The polymer was a brown powder with a softening point of 140° and $\bar{M}_n$ of 1650 (VPO). This is in contrast to a recent preliminary study[2] of the polymerization characteristics of **1**,

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