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Influence of Temperature and Polarity of the Medium on Rate and Equilibrium Constants in the Cationic Polymerization of Tetrahydrofuran

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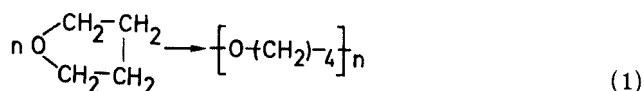
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ABSTRACT

The propagation step of the polymerization process of tetrahydrofuran was studied in detail. The influence of temperature and dielectric constant of the reaction medium on the rate and equilibrium constants of the elementary steps of the reaction was investigated. As the changes of temperature result in changes of the dielectric constant of the medium, it was found necessary to give the dependence of the reaction constants on both these parameters simultaneously.

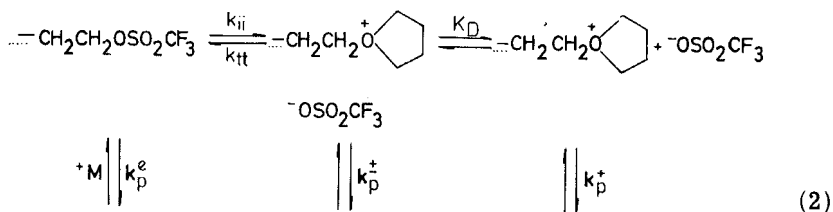
INTRODUCTION

Understanding of the propagation step in a polymerization process involves, first of all, the determination of the corresponding rate and equilibrium constants describing this particular reaction. Thus in the cationic polymerization of tetrahydrofuran (THF) which gives the linear polyether chain



one has to determine the rate constants of all elementary reactions involved in the propagation step.

These reactions, in agreement with the formalism developed by us earlier [1-4] are shown in Eq. (2):



where

$$k_{ii}/k_{tt} = K_E \text{ and } k_p^\pm = k_p^+ = k_p^I$$

Rate constants and equilibrium constants listed in Eq. (2) have been recently determined in our laboratory for various solvent/monomer mixtures at various temperatures [1-6]. The present paper discusses the influence of the simultaneous changes of polarity of the reaction medium (expressed by macroscopic dielectric constant ϵ) and temperature T on the rate constants and equilibrium constants.

THE TWO-PARAMETER EQUATION

The influence of temperature on the rate constants can generally be expressed by the Arrhenius equation

$$k = A' \exp \{ B'/T \} \quad (3)$$

It follows from the Eyring theory of the transition state, that A' and B' can be expressed through the entropy ΔS^\ddagger and enthalpy ΔH^\ddagger of activation

$$A' = (k T/h) \exp \{ \Delta S^\ddagger / R \} \quad (3a)$$

$$B' = -\Delta H^\ddagger / RT \quad (3b)$$

In Eqs. (3a) and (3b) h denotes Planck's constant, k is Boltzmann's constant, and R is the gas constant. For the equilibrium constant K , A' and B' have the following meaning

$$A' = \exp \{ \Delta S_e / R \} \quad (3c)$$

$$B' = -\Delta H_e / R \quad (3d)$$

where ΔS_e and ΔH_e are the equilibrium entropy and enthalpy respectively. Other important factors, influencing rates and equilibria of chemical reactions, are so called "medium effects". The polarity, polarizability, basicity and acidity of the solvent are here of primary importance.

In multicomponent systems determination of basicity or acidity of reaction mixture is very difficult. Dielectric constant is the parameter most often used. In multicomponent mixtures the macroscopic dielectric constant is usually a molar additive function of the dielectric constants of each component.

According to different theories, $\ln K$ depends linearly on certain dielectric functions. The most often used expressions [7] are: ϵ^{-1} , $(\epsilon - 1)/(2\epsilon + 1)$, $(\epsilon - 1)/(\epsilon + 2)$, $(\epsilon - 1)/(\epsilon + 1)$. Among all of these functions there exists a linear correlation for sufficiently small changes of ϵ . Thus, the choice between different formally equivalent functions is only arbitrary. In the present paper the simplest one was applied

$$K = C' \exp \{ D' / \epsilon \} \quad (4)$$

where C' and D' are empirical constants. Equation (4) can be used for rate as well as equilibrium constants.

In our earlier work [4] we have used as solvents several derivatives of methane: nitromethane (CH_3NO_2), methylene dichloride (CH_2Cl_2), and carbon tetrachloride (CCl_4). These compounds differ mainly in dielectric constant, although their basicities are also different. Assuming, that the dielectric constant is a prevailing factor our further discussion will be limited to the influence of polarity of the reaction mixture on the equilibrium and rate constants. Equations (3) and (4) can be combined, giving new equation in which both parameters ϵ and T are considered:

$$\ln k = A + (B/T) + (C/\epsilon) + (D/\epsilon T) \quad (5)$$

At constant temperature T_c , $A + (B/T_c) = \ln C'$ and $C + (D/T_c) = D'$.

When dielectric constant is kept unchanged and temperature is varied (in some cases isodielectric [8] mixtures were used) we eventually obtain $A + (C/\epsilon_c) = \ln A'$ and $B + (D/\epsilon_c) = B'$. Having determined A' , B' , C' , and D' at different conditions (ϵ and T were changed), we can calculate all the parameters from Eq. (5). Equation (5) can be re-written in a different form

$$\ln k = \ln k_0 + a \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (6)$$

where $a = D$, $\epsilon_0 = -D/B$, $T_0 = -D/C$ and $\ln k_0 = A - (BC/D)$. In Eq. (6), a stands for the susceptibility of k to dielectric constant and temperature. When $a > 0$, then with increase of ϵ the enthalpy of activation increases, and/or with increase of temperature the reaction rate constant becomes more dependent on dielectric constant. When, however, $a < 0$, then the opposite is true. For $a = 0$ the rate constant k is influenced neither by dielectric constant nor by temperature. T_0 is the isokinetic temperature. When passing T_0 the dependence of $\ln k$ on ϵ becomes reversed and exactly at $T = T_0$ the rate constant does not depend on polarity of the system. ϵ_0 is the isokinetic dielectric constant; at $\epsilon = \epsilon_0$ rate constants do not depend on temperature ($\Delta H^\ddagger = 0$).

GRAPHICAL REPRESENTATION OF THE TWO-PARAMETER EQUATION

Experimental data for the calculations were taken from our earlier works, recently summarized [4]. The numerical computations were performed with a Pdp-11 computer.

Equation (6) is an equation of a hyperbolic paraboloid when $(\epsilon^{-1} - \epsilon_0^{-1})$ and $(T^{-1} - T_0^{-1})$ are plotted on the x, y axis and $(\ln k - \ln k_0)$ on the z axis. The geometrical visualization of Eq. (6) is shown in Fig. 1 for different values of a . The next two figures show the surfaces computed for different reaction rate and equilibrium constants. Figure 2a shows the data obtained for rate constants of covalent and

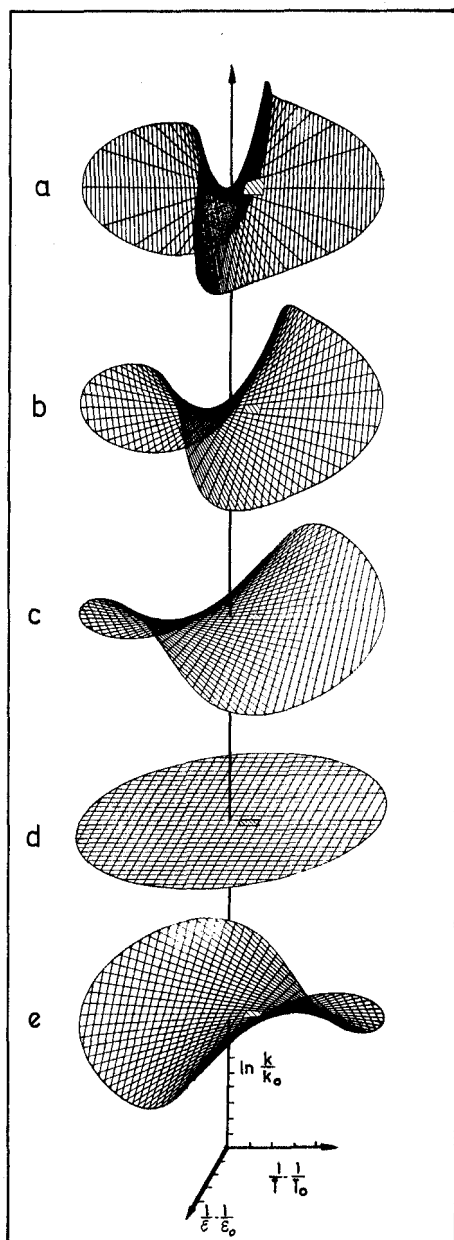
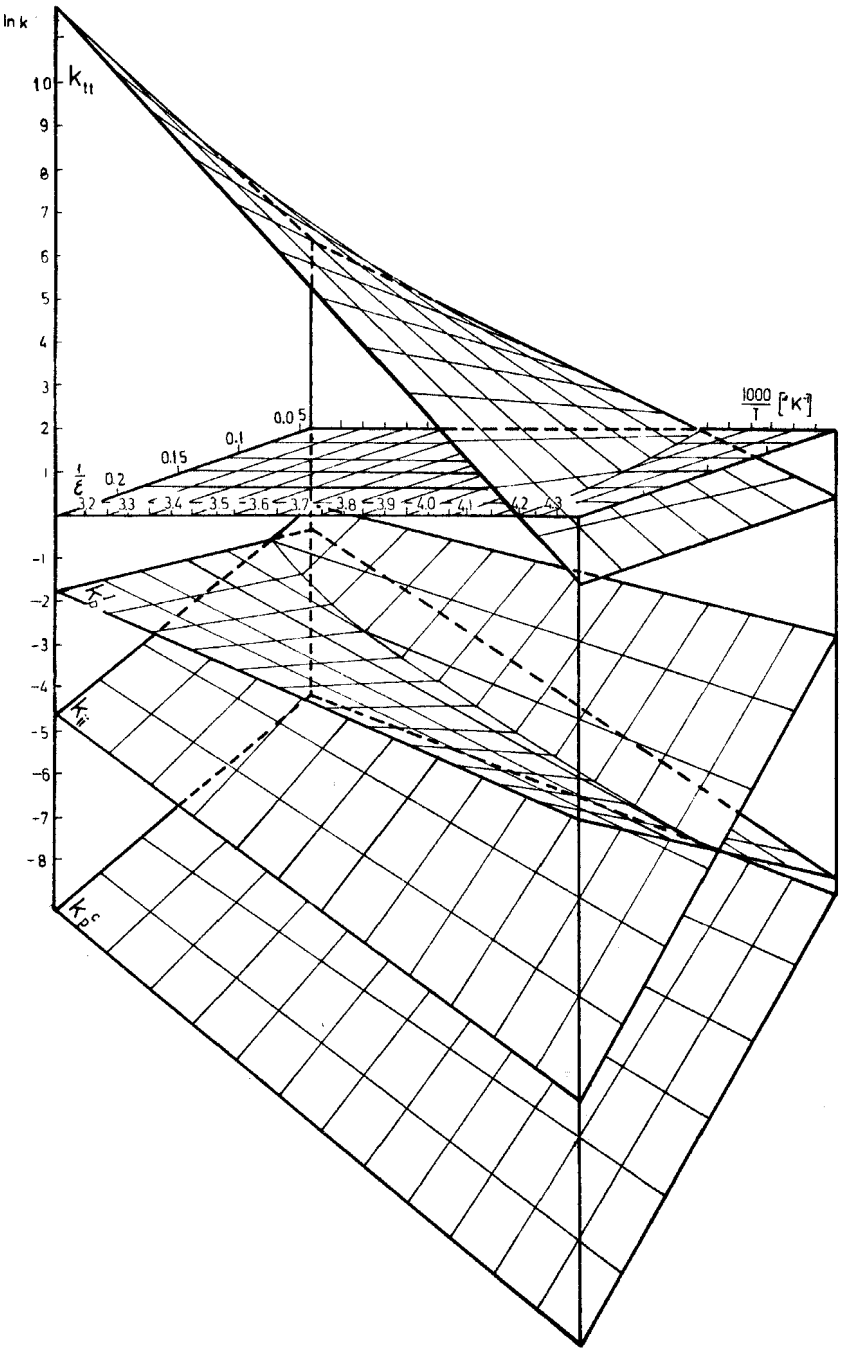


FIG. 1. Geometrical visualization of Eq. (6) for a series of values of the parameter a : (a) $a = 10^5$, (b) $a = 5 \times 10^4$, (c) $a = 2 \times 10^4$, (d) $a = 0$; (e) $a = -2 \times 10^4$ (in arbitrary units). The graphs are plotted in reduced variables $\ln(k/k_0)$, $[(1/T) - (1/T_0)]$, and $[(1/\epsilon) - (1/\epsilon_0)]$ (in arbitrary units). The shaded parts correspond to the ranges of variables T and ϵ in which the experiments were performed, and are magnified in Figs. 2a and 2b. For clarity the graphs are displaced from the coordinate origin along the $\ln(k/k_0)$ axis.

(a)



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(b)

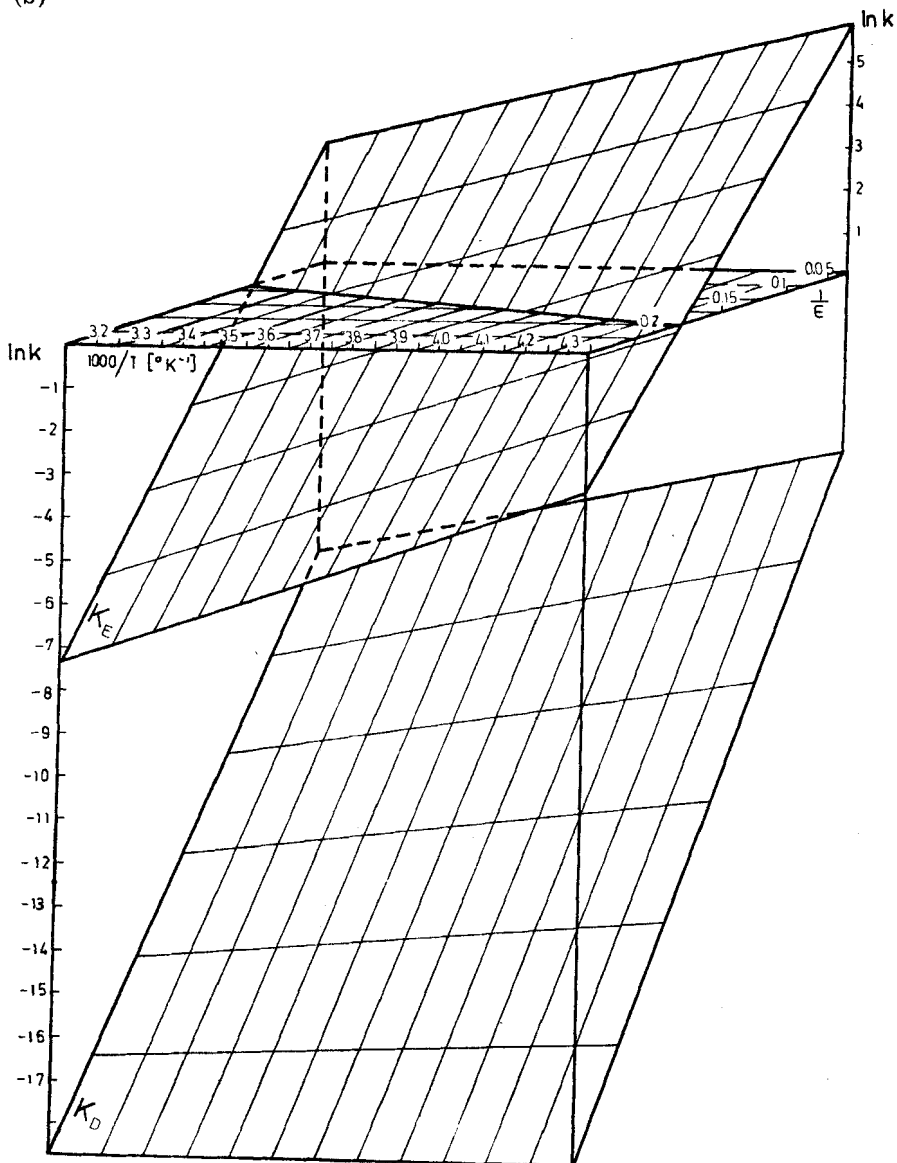


FIG. 2. The dependence of (a) the experimental rate constants k_p^C , k_p^I , k_{tt} , and k_{ii} and (b) equilibrium constants K_D and K_E on temperature and dielectric constant. To find any value of k from the plot one should locate the point of given coordinates $1/\epsilon$ and $1/T$ at the $(1/\epsilon) - (1000/T)$ plane and then measure the distance from that point to the specified surface (k_p^C , k_p^I , k_{tt} , etc.). The grid at the coordinate plane is equivalent to that at the k -surfaces, allowing one to locate the given point.

ionic propagation (k_p^C and k_p^I) as well as for temporary termination (k_{tt}) and internal ionization (k_{ii}) [see also Eq. (2)]. Figure 2b shows data computed for equilibrium constants for dissociation (K_D) and ester-ion equilibrium (K_E). All these surfaces are drawn only in the studied region of changes of dielectric constant and temperature (namely ϵ from 5 to 20 and T from 240 to 310°K). Some of the surfaces are almost flat but others are concave or convex, depending on the sign of a . The data presented in Table 1 characterize the influence of changes of temperature and dielectric constant on the rate or equilibrium constants. Thus, the rate constants are much more sensitive than the equilibrium constants to the changes of the temperature and dielectric constant ($|a|$ for the rate constants is higher). A negative sign of a for k_{ii} , k_{tt} , and k_p^C indicates that with increase of dielectric constants the enthalpy of activation for those reactions decreases. The reverse is true for ionic propagation. Enthalpy of equilibrium between covalent and ionic species is negative (reaction is exothermic). A positive value of a means that with increase of ϵ the ΔH_e also increases (becoming less negative in more polar medium). The value of a is negative for dissociation of ions pairs (K_D), and when ϵ increases, ΔH_D decreases, becoming more negative.

Values of ϵ_0 for almost all the rate constants are less than 1 (dielectric constant of a vacuum). It indicates that in real systems ($\epsilon > 1$), the enthalpy of activation is positive (with increase of temperature rate constants also increase). For ionic propagation, $\epsilon_0 = 1.5$. This means that if ϵ were equal to ϵ_0 , the reaction would proceed with zero activation energy (its rate does not depend on temperature), and in medium of $\epsilon < \epsilon_0$ a decrease of k_p^I with increasing temperature should be observed. The reason for this unusual result can only be the invalidity of Eq. (4) for a medium of low polarity. Indeed, in solvents of low polarity, deviation from predicted linearity is observed.

The isokinetic dielectric constant (ϵ_0) for dissociation of ion-pairs is equal to $\epsilon_0 = 2.6$. Such a value means that at this point we have zero equilibrium enthalpy and in certain ranges of ϵ and T , given by $\ln K_D > a [(1/\epsilon) - (1/\epsilon_0)] [(1/T) - (1/T_0)]$, the dissociation would be endothermic. In spite of the possible uncertainty of this result [invalidity of Eq. (4) may arise as for k_p^I], such a finding can be expected. Exothermicity of dissociation of ion pairs results from

TABLE 1. Values of A, B, C, D Constants from Eq. (5) and $\ln k_0$, a , ϵ_0 , T_0 from Eq. (6) for Different Temperature and Equilibrium Constants in the Polymerization of THF

Constant	A	B	C	D	$\ln k_0$	a	ϵ_0	T_0 ($^{\circ}\text{K}$)	Measurement	
									ϵ	T
I	+ 3.205	-1453	+ 62.48	-24180	- 0.549	-24180	-16.641	+387.00	6-10	24
II	+ 5.584	-3729	+124.50	-28600	-10.649	-28600	- 7.670	+229.72	6-10	24
C	+ 3.369	-2883	+ 54.40	-21980	- 3.766	-21980	- 7.624	+404.04	4-22	27
I	+19.620	-7064	- 31.34	+10930	- 0.635	+10930	+ 1.547	+348.76	4-22	27
E	- 2.406	+2282	- 61.82	+ 4369	+29.884	+ 4369	- 1.915	+ 70.67	4-22	24
D	-10.59	+2160	- 45.49	- 5562	-28.256	- 5562	+ 2.575	-122.30	6-22	25

solvation phenomena which can be neglected in low-polarity solvents, which are poor solvating agents.

Values of T_0 indicate at which temperature the rate or equilibrium constants are independent on changes of dielectric constant. When $T < T_0$, $a < 0$, and $\epsilon_0 < 0$, the rate constants increases with increase of ϵ (k_{ii} and k_p^I). When both a and ϵ_0 are negative but $T > T_0$, the rate constants decrease with increase of ϵ (k_{tt}).

Knowledge of all of the four parameters from Eq. (5) or (6) allows the determination of any constant of interest for any conditions of polarity and temperature using the equations derived.

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