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KINETICS OF RADICAL POLYMERIZATION. LI. INVESTIGATION OF THE RADICAL BULK POLYMERIZATION OF VINYL ACETATE BY THE ROTATING SECTOR METHOD AT DIFFERENT TEMPERATURES

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ABSTRACT

The absolute values of the chain propagation and termination rate coefficients of VAc radical polymerization were determined at 30, 35, 40, and 50°C. Based on these results, the following Arrhenius equations were obtained:

$$k_2 = 1.30 \times 10^9 \exp\left(-\frac{35,162}{RT}\right)$$

and

$$k_4 = 1.64 \times 10^{10} \exp\left(-\frac{14{,}232}{RT}\right)$$

The calculated activation energies of the elementary reaction steps are compared to the literature data, and the differences are discussed.

INTRODUCTION

In a previous paper [17] we dealt with the determination of absolute rate constants of chain propagation (k_2) and termination (k_4) of the radical bulk polymerization of vinyl acetate (VAc) by the rotating sector method at 25°C. The rate constant determined by us are, considering the error of the measuring method, in good agreement with the literature data measured at 25°C.

As regards the activation energies of propagation (E_2) and termination (E_4) elementary steps of the radical VAc polymerization, few data can be found in the literature. The majority of authors [2–5] assume the activation energy of the termination step to be zero ($E_4 = 0$) or very near to zero ($E_4 < 1$). The activation energy values of the chain propagation step are rather scattered and vary between 13.4 kJ/mol [3] and 39.3 kJ/mol.

The aim of the present work is to measure the absolute rate constants of chain propagation (k_2) and termination (k_4) at 30, 35, 40, and 50°C; that is, to determine the temperature dependence of the rate constant and from that to determine the activation energies of the elementary reaction steps.

EXPERIMENTAL

The monomer used was a Fluka product. It was purified and prepolymerized as given in a previous paper [17]. The benzoin used for the rotating sector measurement was a Fluka product as well; it was sometimes recrystallized from ethanol before use. It melted at 135–136°C.

The rotating sector measurements were carried out as described in Ref. 17. The data were evaluated by computer, and the absolute rate constants were determined as given in Refs. 7, 8, and 17.

EXPERIMENTAL RESULTS

The sector curve determined at 40°C is illustrated by Fig. 1. The polymerization rates measured at steady illuminations at different temperatures, as well as the radical lifetimes determined from the sector curves, are, together with the corresponding values, listed in Table 1. In order to avoid local overheating [6], the amount of photoinitiator was decreased at higher temperatures. In our measurements the monomer conversion never exceeded 3%.

The k_2/k_4 quotient can be determined from the data supplied by the rotating sector method by the relationship

$$\frac{k_2}{k_4} = \frac{W_{\text{stac}}}{m}\tau \qquad (1)$$

Absolute rate constants (k_2, k_4) can be determined from the $k_2/\sqrt{k_4}$ rate

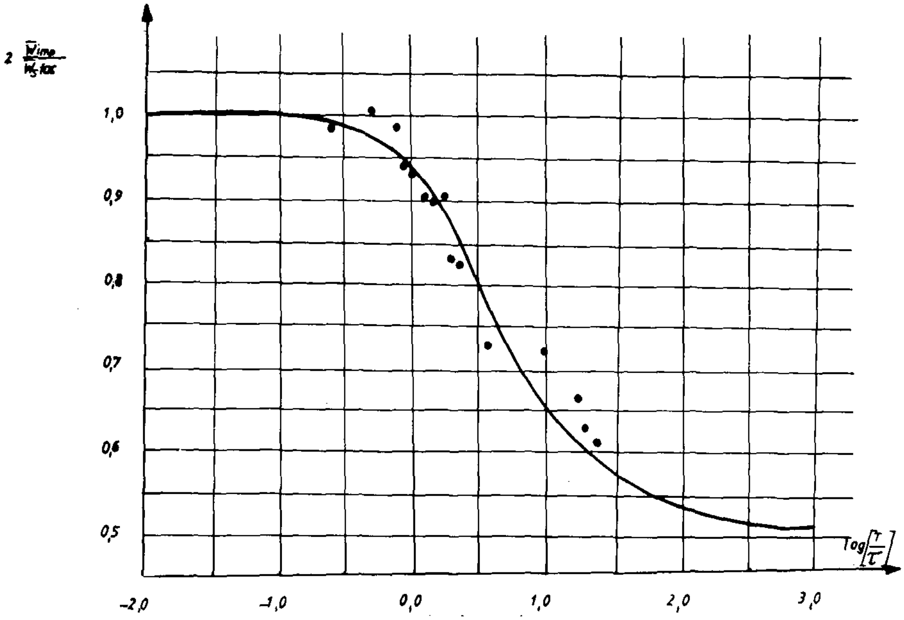

FIG. 1. Fitting of relative radical concentrations determined with different illumination times at 40°C to the theoretical sector curve (sector ratio: $p = 3$, $\tau = 0.429$ s).

TABLE 1. The Rate of VAc Polymerization Measured at Different Temperatures and at Constant Illumination. The Relevant Radical Lifetimes Are Also Indicated

T, °C	$W_{st} \times 10^4$, mol/L·s	ΔW_{st}, %	τ, s	$\Delta\tau$, %	Number of measuring points
25[a]	6.590	0.630	0.247	14.9	17
30	3.380	0.707	0.572	15.3	10
35	3.840	0.707	0.590	15.3	12
40	6.900	0.630	0.429	14.9	16
50	2.690	0.630	1.293	14.9	15

[a] From Ref. 17.

constant available from steady-state kinetics by using the following equations:

$$k_2 = \frac{(k_2/\sqrt{k_4})^2}{k_2/k_4} \tag{2}$$

and

$$k_4 = \left(\frac{k_2/\sqrt{k_4}}{k_2/k_4}\right)^2 \tag{3}$$

For the determination of $k_2/\sqrt{k_4}$ values, the equation describing the temperature dependence of the overall rate constant (K_O) is given in Ref. 1:

$$K_O = 1.35 \times 10^{11} \exp(-90{,}000/RT)\ \mathrm{L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}} \tag{4}$$

was applied together with the Hook-Tobolsky equation [18] to give the temperature dependence of the thermal decomposition of AIBN:

$$k_1 = 1.58 \times 10^{15} \exp(-128{,}930/RT)\ \mathrm{s^{-1}} \tag{5}$$

The $k_2/\sqrt{k_4}$ values can be calculated by the equation

$$\frac{k_2}{\sqrt{k_4}} = \frac{K_O}{\sqrt{2k_1 f}} \tag{6}$$

where $f = 0.536$ is the radical efficiency factor, independent of the temperature [1].

The absolute rate constants determined in this way are listed in Table 2 together with the corresponding error intervals.

The temperature dependences of the chain propagation and termination rate constants (k_2 and k_4) are illustrated by Figs. 2 and 3 in a ln k vs $1/T$ representation. In the figures, the literature values falling in the order of magnitude of those determined by us are shown. The equations of the straight lines fitted to the experimental points are as follows:

$$k_2 = 1.30 \times 10^9 \exp(-35{,}162/RT) \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \tag{7}$$

and

$$k_4 = 1.64 \times 10^{10} \exp(-14{,}232/RT) \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \tag{8}$$

EVALUATION OF THE EXPERIMENTAL RESULTS

The absolute rate constants of elementary steps of VAc bulk polymerization are collected in Table 2. The rate constants determined by investigations using different methods of initial nonsteady-state kinetics are listed in Table 3.

The k_2/k_4 values are within an order of magnitude while the individual values of k_2 and k_4 show considerable differences. The values determined by Dixon-Lewis [3] are especially high. This may be due to several factors, one of which is the insufficient purification of the monomer. Comparison of data is made difficult because the authors have not provided error estimates for the rate constants.

As mentioned above, few data concerning activation energies of the elementary steps of VAc polymerization can be found in the literature. These data are collected in Table 4.

The bimolecular recombination of a highly reactive macroradical like vinyl acetate does not require chemical activity; however, the energy requirement of the corresponding transport process cannot be neglected. The fact that some authors [2–4] assume the activation energy of chain termination to have a value near zero is equivalent to neglecting the diffusional translation energy of the macroradical.

TABLE 2. The Absolute Propagation and Termination Rate Constants of VAc Polymerization at Different Temperatures

T, °C	$(k_2/k_4) \times 10^5$	$k_2/\sqrt{k_4}$,[a] $L^{1/2} \cdot mol^{-1/2} \cdot s^{-1/2}$	$k_2 \pm \Delta k_2$, $L \cdot mol^{-1} \cdot s^{-1}$	$(k_4 \pm \Delta k_4) \times 10^7$, $L \cdot mol^{-1} \cdot s^{-1}$
25[b]	1.506	0.107	756 ± 163	5.02 ± 1.86
30	2.313	0.126	1218 ± 262	5.27 ± 1.95
35	2.093	0.149	1316 ± 283	6.29 ± 2.33
40	2.731	0.175	1830 ± 394	6.70 ± 2.48
50	3.365	0.237	2697 ± 580	8.01 ± 2.96

[a] Calculated by Eq. (1).

[b] From Ref. 1.

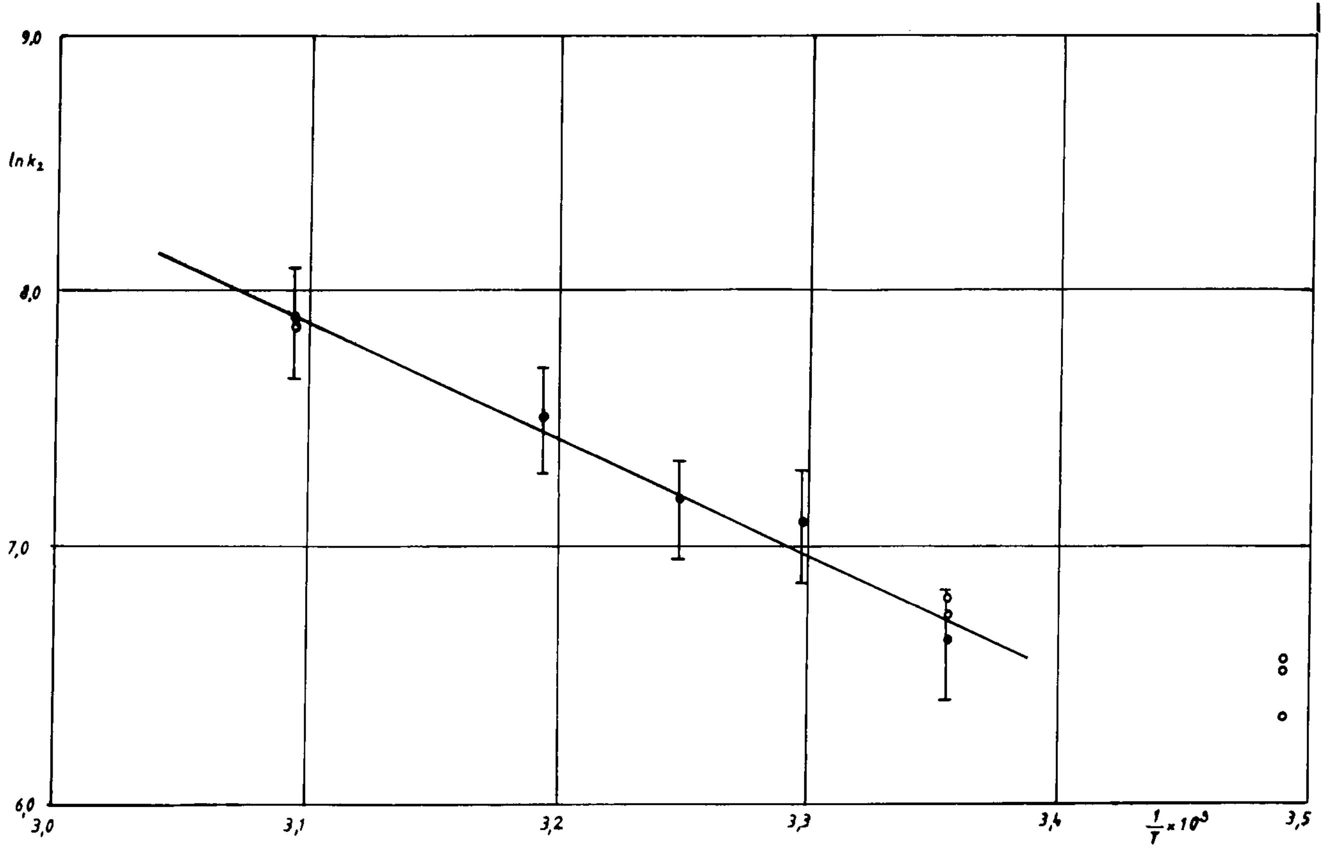

FIG. 2. Temperature dependence of the absolute propagation rate constant of radical VAc polymerization. Literature values determined by the rotating sector methods are indicated by open circles.

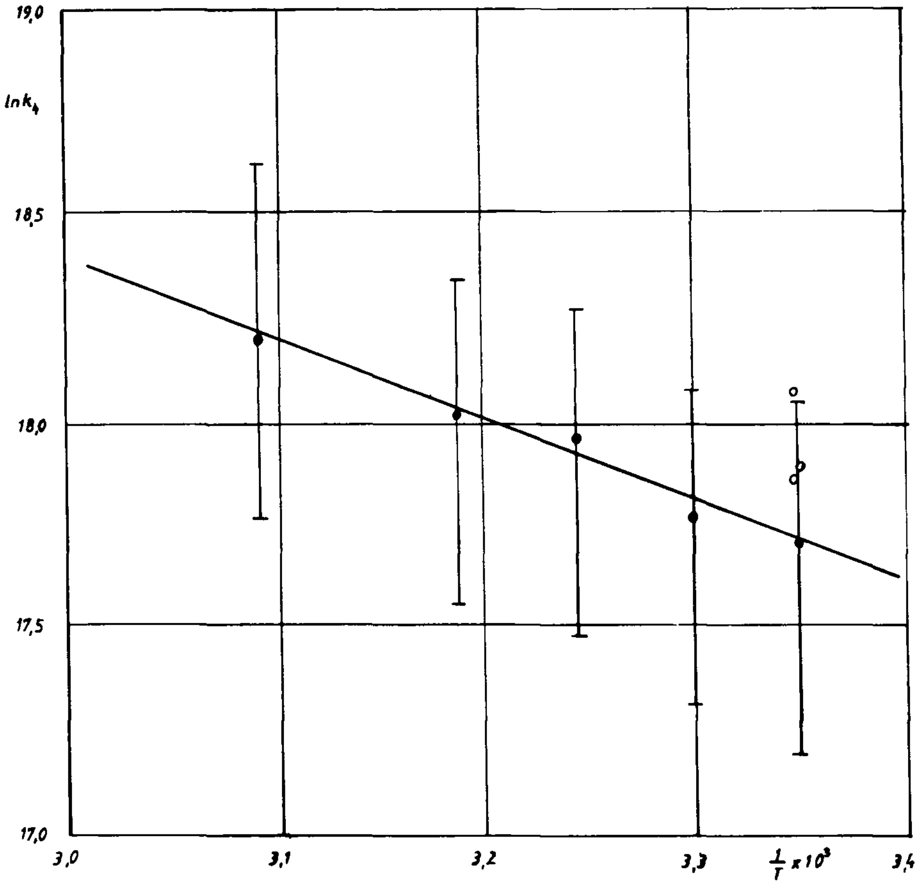

FIG. 3. Temperature dependence of the absolute termination rate constant of radical VAc polymerization. Literature values determined by the rotating sector method are indicated by open circles.

In Ref. 1, 10,046 J/mol was obtained for the activation energy of the chain termination when the transport processes were considered, while the activation energy of propagation was found to be 30,560 J/mol. These values are in good agreement with those reported in this paper (E_2 = 35,162 ± 2,000 J/mol, E_4 = 14,232 ± 5,618 J/mol) when the error of determination estimated from the error interval of rate constants is considered. The equality of activation energy as determined by two dif-

TABLE 3. Literature Data of Absolute Propagation and Termination Rate Constants of VAc Polymerization, Measured by Diverse Methods

k_2, L · mol^{-1} · s^{-1}	$k_4 \times 10^{-6}$, L · mol^{-1} · s^{-1}	$(k_2/k_4) \times 10^{-6}$	T, °C	Measuring method literature
2000	220	9.09	0	Viscometry [4]
2600	220	11.82	0	Viscometry [4]
–	–	3.10	15	Initial nonsteady-state kinetics (dielectric constant) [10]
–	–	20.0	15	Initial nonsteady-state kinetics (interferometry) [11]
–	–	26.0	16	Initial nonsteady-state kinetics (thermoelement) [12]
559	51.8	10.80	20	Initial nonsteady-state kinetics (termistor) [13]
895	24	37.20	25	Initial nonsteady-state kinetics (thermoelement at 4% conversion) [4]

TABLE 4. Literature Data of Activation Energies of the Propagation and Termination Elementary Steps of VAc Polymerization

E_2, kJ/mol	E_4, kJ/mol	Literature
18.48	0	3
30.64	21.94	17
13.39	0	4
16.58	4.18	5
39.35	–	7
35.15	14.23	Present work
30.56	10.05	2

ferent methods, especially with regard to the elementary step of termination, proves that the transport process must to be taken into account.

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