

Reactions of Trithiocyanuric Acid with Oxiranes.

II. Kinetics and Mechanism of Reactions

MIECZYŚLAW KUCHARSKI, ELŻBIETA CHMIEL-SZUKIEWICZ

Department of Organic Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

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ABSTRACT: The study of the kinetics of the addition of trithiocyanuric acid to oxiranes (i.e., ethylene oxide and propylene oxide) in DMSO solution in the presence of triethylamine as a catalyst is described. The effects of the acid group concentration, the concentration of oxirane, and the catalyst on the course of the reaction was studied. The rate equation describing the addition was derived. The reaction order with respect to the oxirane, catalyst, and reactive groups of the acid were 0.5, 0.5, and 1.5, respectively. The mechanism of addition was proposed. The influence of temperature on the course of the reaction was also studied. The activation parameters (ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) were calculated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2081–2088, 2000

Key words: trithiocyanuric acid; oxiranes; addition; kinetics; reaction mechanism

INTRODUCTION

The methods of preparation of polyetherols with an *s*-triazine ring in reactions of trithiocyanuric acid with oxiranes such as ethylene oxide (EO) or propylene oxide (PO) were presented in a previous article.¹ The syntheses were carried out with a large excess of oxirane in DMF solution and in the presence of triethylamine (TEA) as the catalyst. To our knowledge the compositions of reaction products of trithiocyanuric acid with oxiranes and the courses of these reactions have not been reported so far, which is in contrast to reactions of oxiranes with other compounds containing active hydrogen atoms such as alcohols,^{2–7} phenols,⁸ thiols,^{9–11} carboxylic acids,^{12–16} amines,^{17–20} amides,^{21,22} or imides.²³

This article reports on attempts to establish the kinetics and mechanism of reactions carried out during the addition of trithiocyanuric acid to oxiranes. The conditions applied were similar to

those used in the preparation of other polyetherols.

EXPERIMENTAL

Kinetics Measurements

A calculated amount of trithiocyanuric acid (pure, Aldrich, Germany) was weighed carefully (to within ± 0.0001 g) into a 50-mL measuring flask. The flask was then filled with about 30 mL of DMSO (pure, Sigma), heated until the trithiocyanuric acid dissolved, and then cooled down. Portions of the TEA catalyst (pure, Fluka, Switzerland) and oxirane (EO or PO, pure, Fluka) were then introduced and the flask filled to the mark with preheated DMSO.

The measurements were carried out in a glass dilatometer of about 45-mL capacity, which was equipped with a capillary of 40-cm length and 0.1-cm inner diameter. The time was recorded starting from the moment of mixing the reagents. The first reading was usually made after 15–20 min. This time was required to fill the dilatometer

Correspondence to: M. Kucharski.

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Table I Rate Constants of Addition of Trithiocyanuric Acid to EO at 40°C

$c_{0\text{AH}}$ (mol/L)	Molar Ratios of Reactive Groups AH : EO	n	$k \times 10^5$ (mol ^{1/2} /L ^{1/2} /s)	$k' \times 10^5$ (L/mol/s) Calcd from eq. (6)	$k' \times 10^5$ (L/mol/s) Calcd from eq. (8)	$k'' \times 10^5$ (L ^{3/2} /mol ^{3/2} /s)
1.5000	6.00 : 1.00	0.41 ± 0.10	1.87 ± 0.04	1.02 ± 0.02	1.10 ± 0.03	3.48 ± 0.09
1.2000	4.80 : 1.00	0.47 ± 0.09	1.49 ± 0.02	1.13 ± 0.02	1.24 ± 0.03	3.94 ± 0.09
0.9900	3.96 : 1.00	0.56 ± 0.12	1.04 ± 0.02	1.06 ± 0.02	1.20 ± 0.03	3.79 ± 0.09
0.7500	3.00 : 1.00	0.92 ± 0.06	0.82 ± 0.02	1.26 ± 0.03	1.48 ± 0.01	4.68 ± 0.04

$$c_{0\text{B}} = 0.25 \text{ mol/L}; c_{\text{K}} = 0.10 \text{ mol/L.}$$

and stabilize the temperature. Further readings were made in increasing time intervals (from 5 min up to a few hours) until a constant meniscus level in the capillary was attained.

The relative concentration of oxirane was calculated assuming all volume changes to be due to oxirane consumption.

Determination of the reaction order (n) and rate constant (k) were carried out to obtain the best fit of experimental results using the least squares method.

The Gibbs activation energy (ΔG^\ddagger) was calculated using the following equation:

$$\Delta G^\ddagger = RT \cdot \left(23.764 - \ln \frac{k}{T} \right) \quad (1)$$

where k and R are the reaction rate constant and gas constant, respectively. The plot of ΔG^\ddagger against temperature (T) gave a straight line that yielded the activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of the reaction.

Analytic Methods

Elemental analysis of the trithiocyanuric acid-TEA adduct (C, H, N, S) was performed using an EA-1108 analyzer (Fisons, Italy). The IR spectrum was recorded on a Fourier transform IR Paragon 1000 spectrometer (Perkin-Elmer Corp., Norwalk, CT). The sample for IR analysis was prepared in the form of a KBr tablet. The ¹H-NMR spectrum of the trithiocyanuric acid-TEA adduct was recorded on an 80-MHz BS-586A spectrometer (Tesla, Czechoslovakia). The solvent was *d*₆-DMSO with an HMDSO internal standard. The changes in the conductivity of trithiocyanuric acid-TEA solutions were recorded using an OK-102/1 conductometer (Radelkis, Hungary).

RESULTS AND DISCUSSION

The aims of studying the kinetics of reactions of trithiocyanuric acid with oxiranes were to develop the general rate equation for the addition of trithiocyanuric acid to oxiranes, to propose the mechanism of reaction, and to determine activation parameters.

The dilatometric method was used to study the kinetics of the addition of trithiocyanuric acid to oxiranes because the operating conditions of this reaction (TEA as catalyst, small oxirane concentrations) were not suitable to apply the direct concentration measurement technique. The temperature of the reaction was always kept sufficiently low to limit the volatility of the oxiranes. Investigations were carried out in DMSO solution, because DMSO dissolves trithiocyanuric acid relatively well. The largest concentration of acid was only 0.5 mol/L because of its limited solubility.

At first the rate equation describing the reaction course was found. The approximate value of the reaction order (n) with respect to the oxirane concentration was determined using the following general relationship:

$$-\frac{dc_{\text{B}}}{dt} = k \cdot c_{\text{B}}^n \quad (2)$$

where c_{B} is the oxirane concentration (mol/L) and k is the reaction rate constant (mol^{1- n} /L^(1- n)/s).

The order n that was equal to 0.5 provided the best fit. (It was valid for at least a fourfold excess of acid reactive groups with respect to oxirane, cf. Table I.) The rate equation was thus modified to the following form:

$$-\frac{dc_{\text{B}}}{dt} = k \cdot c_{\text{B}}^{1/2} \quad (3)$$

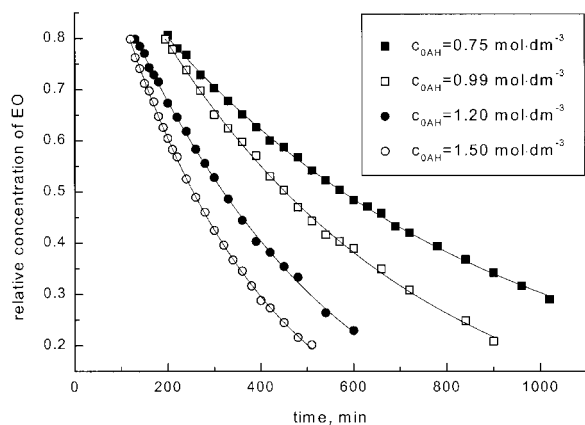
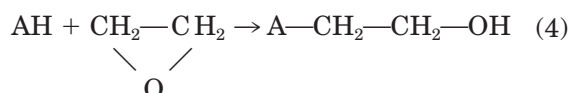


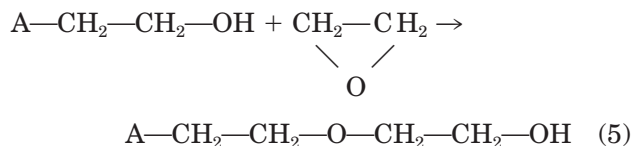
Figure 1 The time dependence of the relative concentration of EO and the effect of the concentration of trithiocyanuric acid.

and the reaction rate constant was calculated (see Table I).

The addition reaction can be formally split into two steps: the reaction between AH and EO,



and the reaction between newly formed hydroxyethyl groups and oxirane (the consecutive reaction),



To limit the second reaction, an excess of —SH groups with respect to oxirane should be applied; under this condition, because of the large reactivity of the —SH groups with respect to newly formed hydroxyethyl ones, the mentioned consecutive reaction can be neglected. Thus, the rate constant in eq. (3) can be expressed as

$$k = k' \cdot c_{\text{AH}}^n \quad (6)$$

As mentioned earlier, the rate of the reaction of trithiocyanuric acid with EO follows eq. (3). A reaction order (n) equal to 0.5 is applicable to at least a fourfold excess of AH groups with respect to EO (see Table I, Fig. 1). The reaction becomes the first-order one for a threefold excess of AH groups. However, at the initial stage of the reac-

tion a reaction order of 0.5 is observed. Then it rises at a conversion of about 50%. The concentration of groups becomes too small to assume it stays constant throughout.

In the presence of an excess of reactive groups of AH and assuming the reaction is a half-order with respect to oxirane, n and k' can be calculated using eq. (6) (cf. Fig. 2). The rate equation providing the best fit becomes

$$v = k' \cdot c_{\text{AH}}^{3/2} \cdot c_{\text{B}}^{1/2} \quad (7)$$

If the above relationship correctly describes the reaction of trithiocyanuric acid with EO then the reaction constant k' calculated from eq. (6) and the k' appearing in eq. (8) below, where the assumption about the constancy of c_{AH} has not been made, should have approximately the same value.

$$v = k' \cdot (c_{\text{0AH}} - \alpha)^{3/2} \cdot (c_{\text{0B}} - \alpha)^{1/2} \quad (8)$$

where c_{0AH} and c_{0B} are the initial concentration of the reactive groups of AH and oxirane, respectively, and α is the instantaneous concentration of oxirane in the reaction with AH groups that is calculated directly from the dilatometer readout.

The data in Table I confirm that the rate constants calculated from eqs. (6) and (8) have very similar values, even for the threefold excess of reactive groups of AH with respect to EO.

The study on the effect of the catalyst was carried out with the constant reagent concentration ratio set to a threefold excess of reactive groups of AH with respect to EO (cf. Fig. 3). In Table II the rate constants are presented for a

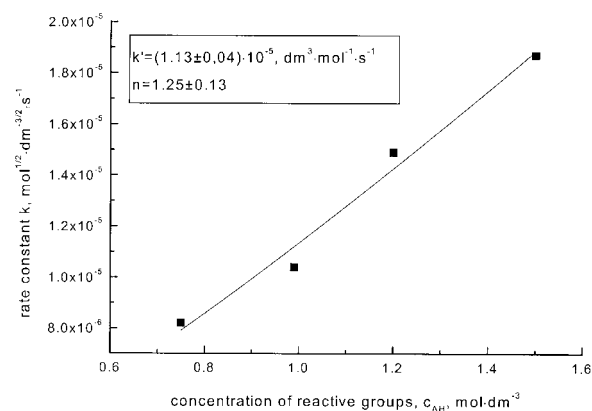


Figure 2 The determination of the reaction order with respect to AH groups for the reaction of trithiocyanuric acid with EO.

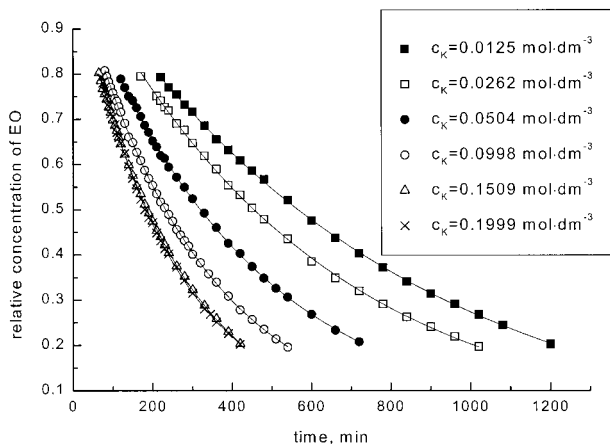


Figure 3 The time dependence of the relative concentration of EO and the effect of the concentration of TEA.

number of rate equations differing in assumed reaction order. The smallest value of the standard deviation was obtained for the equation in the same form as eq. (8). This confirms that eq. (8) is correct within the range of concentrations investigated.

The change in catalyst concentration does not change the reaction order (cf. Table II). The rate constant can be expressed in the following general form:

$$k' = k'' \cdot c_K^m \quad (9)$$

Using this equation one can find the values of m and k'' (cf. Fig. 4).

Hence, the general kinetic equation describing the addition of trithiocyanuric acid to EO has the form

$$v = k'' \cdot c_K^{1/2} \cdot c_{AH}^{3/2} \cdot c_B^{1/2} \quad (10)$$

where

$$c_{AH} = 3 \cdot c_{\text{trithiocyanuric acid}} \quad (11)$$

The values of the reaction rate constant k'' are presented in Tables I and II.

Equation (10) suggests the following mechanism of the reaction in question:

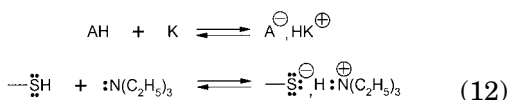


Table II Rate Constants of Addition of Trithiocyanuric Acid to EO at 40°C Calculated for Different Kinds of Kinetic Equations

c_K (mol/L)	n	$v = k'' \cdot c_K^{1/2} \cdot c_{AH}^{3/2} \cdot c_B^{1/2}$	$v = k' \cdot (c_{0AH} - \alpha)^{3/2}$	$v = k'' \cdot c_K^{1/2} \cdot c_{AH}^{3/2} \cdot c_B^{1/2}$					
		$k \times 10^5$ (s ⁻¹)	σ	$k' \times 10^5$ (L/mol/s)	σ	$k'' \times 10^5$ (L ^{3/2} /mol ^{3/2} /s)	σ		
0.0125	0.72 ± 0.05	1.02 ± 0.01	0.011	1.52 ± 0.07	0.030	0.76 ± 0.01	0.011	6.79 ± 0.09	0.011
0.0262	0.79 ± 0.06	1.25 ± 0.02	0.016	1.88 ± 0.08	0.029	0.94 ± 0.01	0.011	5.79 ± 0.08	0.011
0.0504	0.89 ± 0.04	1.81 ± 0.04	0.020	2.66 ± 0.07	0.020	1.35 ± 0.01	0.008	6.03 ± 0.06	0.008
0.0998	0.88 ± 0.04	2.46 ± 0.04	0.020	3.66 ± 0.09	0.021	1.83 ± 0.02	0.009	5.80 ± 0.05	0.009
0.1509	0.89 ± 0.03	3.08 ± 0.06	0.020	4.56 ± 0.11	0.019	2.30 ± 0.02	0.007	5.91 ± 0.05	0.007
0.1999	0.87 ± 0.05	3.09 ± 0.06	0.020	4.27 ± 0.13	0.022	2.31 ± 0.02	0.010	5.16 ± 0.06	0.010
0.3035	0.92 ± 0.04	3.40 ± 0.08	0.022	5.07 ± 0.11	0.019	2.55 ± 0.03	0.010	4.62 ± 0.05	0.010

$c_{0AH} = 1.50$ mol/L; $c_{0B} = 0.50$ mol/L; σ , standard deviation.

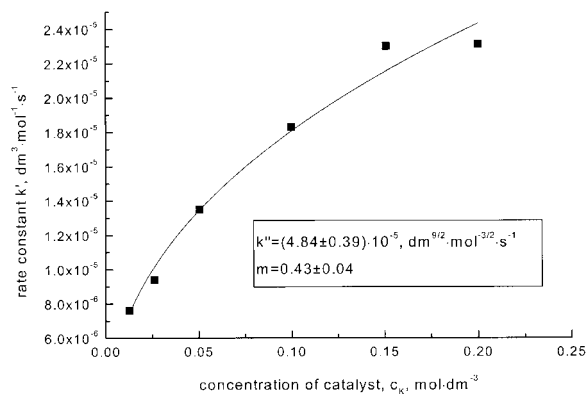
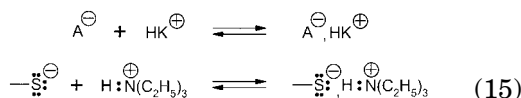
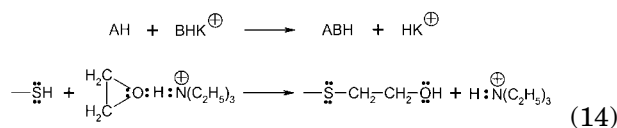
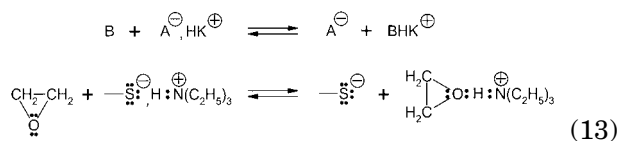


Figure 4 The determination of the reaction order with respect to the catalyst for the reaction of trithiocyanuric acid with EO.



In this mechanism there are four elementary reaction steps:

1. adduct formation with proton transfer from the sulfur atom of trithiocyanuric acid to the nitrogen atom of the catalyst ,

Table III Elemental Analysis of Adduct of Trithiocyanuric Acid with TEA

Element	Weight Composition (%)			
	Found	Calculated for Adduct		
		1 : 1	1 : 2	1 : 3
C	39.98	38.82	47.46	52.46
H	6.61	6.52	8.76	10.06
N	19.68	20.12	18.45	17.48
S	34.38	34.54	25.34	20.00

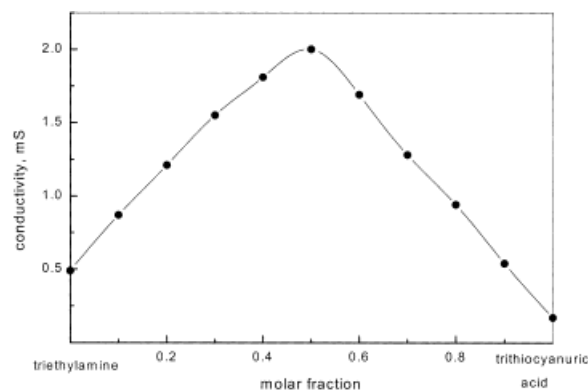
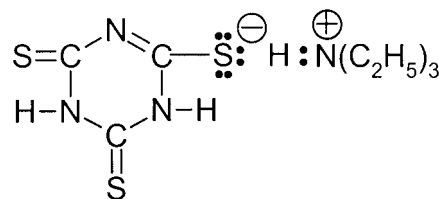


Figure 5 The conductivity of DMSO–water solutions vs. the molar fraction of trithiocyanuric acid.

2. formation of the preactive form of oxirane by hydrogen bonding with a protonized catalyst ,
3. the reaction of the preactive form of oxirane with the —SH groups of trithiocyanuric acid , and
4. reproduction of the adduct of trithiocyanuric acid with TEA .

The adduct of trithiocyanuric acid with TEA was isolated in crystalline form. Its structure was determined by using elemental analysis (cf. Table III), IR, and $^1\text{H-NMR}$ techniques and electrochemistry (cf. Figs. 5–7).



(I)

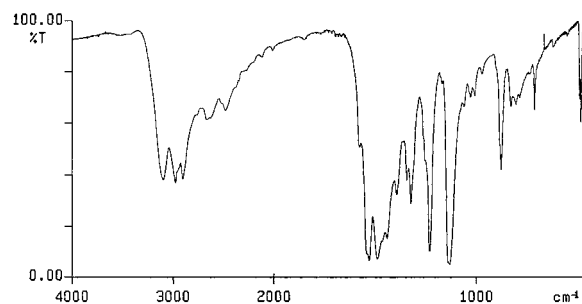


Figure 6 The IR spectrum of the trithiocyanuric acid–TEA adduct.

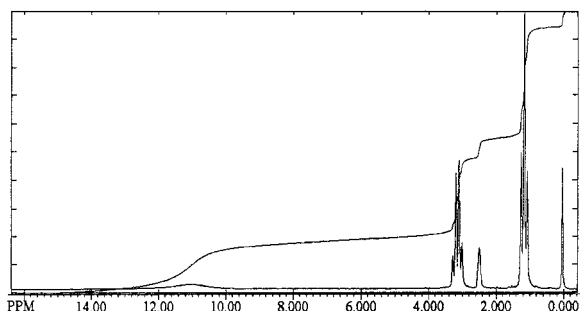


Figure 7 The $^1\text{H-NMR}$ spectrum of the trithiocyanuric acid-TEA adduct.

The elemental analysis shows that in adduct (I) the molar donor : acceptor ratio is 1 : 1. The changes in conductivity of trithiocyanuric acid-TEA solutions confirm this finding. The only maximum on the curve in Figure 5 (conductivity changes L vs. molar fraction x) corresponds to the adduct composition of 1 : 1.

In the $^1\text{H-NMR}$ spectrum of the adduct (Fig. 6), apart from signals from protons of methyl and methylene groups at 1.1 and 3.2 ppm, respectively, the common signal from $-\text{SH}$, >NH , and H:NR_3^+ groups between 10.3 and 12.0 ppm were observed. Broadening of the signal and its shift toward lower values (cf. the $^1\text{H-NMR}$ spectrum of pure trithiocyanuric acid presented in fig. 3 of our previous article¹) show a transfer of protons. The ratio of areas, calculated from the integration curve, is equal to

$$\text{CH}_3:\text{CH}_2:\text{H}(-\text{SH}, \text{>NH}, \text{H:NR}_3^+) = 3:2:1$$

which confirms the anticipated composition of the adduct.

Table IV Rate Constants of Addition of Trithiocyanuric Acid to EO at 40°C

c_{0B} (mol/L)	n	$k \times 10^5$ ($\text{mol}^{1-n}/\text{L}^{(1-n)}/\text{s}$)
0.1249	0.24 ± 0.17	1.11 ± 0.05
0.2500	0.41 ± 0.10	1.87 ± 0.04
0.5037	0.88 ± 0.04	4.93 ± 0.05
1.0012	1.19 ± 0.05	4.39 ± 0.06
1.4994	1.78 ± 0.03	4.13 ± 0.06
2.0024	2.10 ± 0.06	3.26 ± 0.04
2.5036	3.01 ± 0.10	1.40 ± 0.04

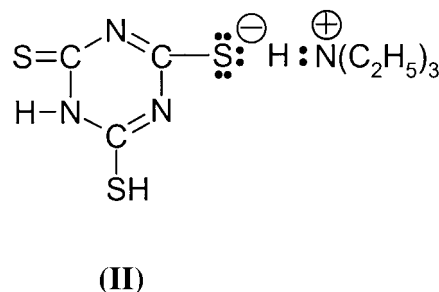
$$c_{0\text{AH}} = 1.50 \text{ mol/L}; c_K = 0.10 \text{ mol/L.}$$

Table V Rate Constants of Addition of Trithiocyanuric Acid to EO: Effect of Temperature

T (K) (°C)	$k'' \times 10^5$ ($\text{L}^{3/2}/\text{mol}^{3/2}/\text{s}$)
303 (30)	2.62 ± 0.03
308 (35)	4.04 ± 0.04
313 (40)	5.80 ± 0.05

$$c_{0\text{AH}} = 1.50 \text{ mol/L}; c_{0B} = 0.50 \text{ mol/L}; c_K = 0.10 \text{ mol/L.}$$

The structure of the solid adduct was also confirmed by its IR spectrum (Fig. 7). The characteristic band due to stretching vibrations of >NH in H:NR_3^+ at $2485\text{--}2666 \text{ cm}^{-1}$ was identified. This band shows that the strategic bond in the adduct has ionic character. In solutions, the dithiolic form of the acid, which is present in the adduct, seems to dominate as follows from the value of its acid number.²⁴



The rate determining step is elementary reaction (14) and thus the overall reaction rate is given by

$$v = v_3 = k_3 \cdot c_{\text{AH}} \cdot c_{\text{BHK}^+} \quad (16)$$

The concentration of the preactive form of oxirane can be calculated from the Bodenstein principle:

$$\frac{dc_{\text{BHK}^+}}{dt} = k_2 \cdot c_B \cdot c_{\text{A}^-, \text{HK}^+} - k_{-2} \cdot c_{\text{A}^-} \cdot c_{\text{BHK}^+} - k_3 \cdot c_{\text{AH}} \cdot c_{\text{BHK}^+} = 0 \quad (17)$$

Because $c_{\text{A}^-} \cong c_{\text{BHK}^+}$, we obtain

$$c_{\text{BHK}^+} = \frac{-k_3 \cdot c_{\text{AH}} + \sqrt{k_3^2 \cdot c_{\text{AH}}^2 + 4 \cdot k_2 \cdot c_B \cdot c_{\text{A}^-, \text{HK}^+} \cdot k_{-2}}}{2 \cdot k_{-2}} \quad (18)$$

Table VI Rate Constants of Addition of Trithiocyanuric Acid to PO: Effect of Temperature

T (K) (°C)	$k'' \times 10^5$ (L ^{3/2} /mol ^{3/2} /s)
308 (35)	2.78 ± 0.02
313 (40)	4.38 ± 0.05
318 (45)	7.01 ± 0.12
323 (50)	10.00 ± 0.07

$$c_{\text{OAH}} = 1.50 \text{ mol/L}; c_{\text{OB}} = 0.50 \text{ mol/L}; c_{\text{K}} = 0.10 \text{ mol/L}.$$

Moreover, because $k_3 \ll k_2$, eq. (18) reduces to

$$c_{\text{BHK}^+} = \frac{\sqrt{4 \cdot k_2 \cdot k_{-2} \cdot c_B \cdot c_{\text{A}^-, \text{HK}^+}}}{2 \cdot k_{-2}} = K_2^{1/2} \cdot c_B^{1/2} \cdot c_{\text{A}^-, \text{HK}^+}^{1/2} \quad (19)$$

where K_2 is the equilibrium constant of reaction (13).

The substitution of eq. (19) into eq. (16) leads to

$$v = k_3 \cdot K_2^{1/2} \cdot c_{\text{AH}} \cdot c_B^{1/2} \cdot c_{\text{A}^-, \text{HK}^+}^{1/2} \quad (20)$$

Furthermore, $c_{\text{A}^-, \text{HK}^+}$ can be calculated from the equilibrium constant

$$K_1 = \frac{c_{\text{A}^-, \text{HK}^+}}{c_{\text{AH}} \cdot c_{\text{K}}} \quad (21)$$

Hence,

$$c_{\text{A}^-, \text{HK}^+} = K_1 \cdot c_{\text{AH}} \cdot c_{\text{K}} \quad (22)$$

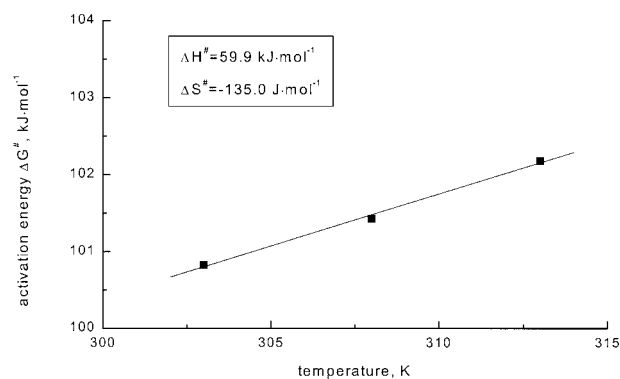
where K_1 is the equilibrium constant of reaction (12).

Substitution of eq. (22) into eq. (20) yields

$$v = k_3 \cdot K_2^{1/2} \cdot c_{\text{AH}} \cdot c_B^{1/2} \cdot K_1^{1/2} \cdot c_{\text{AH}}^{1/2} \cdot c_{\text{K}}^{1/2} = k'' \cdot c_{\text{K}}^{1/2} \cdot c_{\text{AH}}^{3/2} \cdot c_B^{1/2} \quad (23)$$

Table VII Activation Parameters of Reaction of Trithiocyanuric Acid with EO or PO

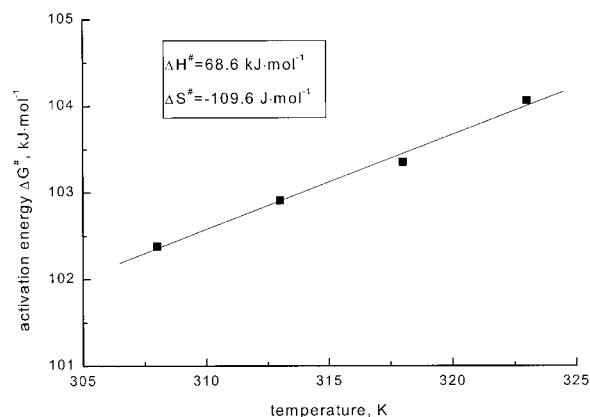
Activation Parameters	EO	PO
ΔG^\ddagger (kJ/mol)	101.5	103.3
ΔH^\ddagger (kJ/mol)	59.9	68.6
ΔS^\ddagger (J/mol/K)	-135.0	-109.6


Figure 8 The activation energy ΔG^\ddagger vs. the temperature for the addition of trithiocyanuric acid to EO.

The relationship derived from the assumed mechanism agrees well with the experimental kinetic data, thus justifying the assumption.

The effect of EO concentration on the reaction course at constant concentrations of trithiocyanuric acid (0.5 mol/L) and TEA (0.1 mol/L) was also investigated. At an increased concentration of oxirane, the contribution from consecutive reactions becomes significant and the reaction changes from the half-order to the third order, as follows from Table IV. Then the rate equation, eq. (10), becomes inapplicable.

The effect of temperature on the addition of trithiocyanuric acid to EO and PO were also investigated (cf. Tables V, VI). It can be shown that eq. (10) derived for EO remains valid for reactions with PO (Table VII). The Gibbs activation energy (ΔG^\ddagger) was calculated from eq. (1) and enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) determined therefrom (cf. Figs. 8, 9). The results are presented in Table VII. The small value of ΔS^\ddagger confirms the bimolec-


Figure 9 The activation energy ΔG^\ddagger vs. the temperature for the addition of trithiocyanuric acid to PO.

ular transition state as suggested by reaction (14). The larger reactivity of EO than PO can be explained by the availability of both carbon atoms to nucleophilic attack. The analysis of experimental data leads to the conclusion that the reactivity of oxiranes with respect to trithiocyanuric acid is determined by enthalpy changes.

CONCLUSIONS

The kinetics of the reaction of trithiocyanuric acid with EO and PO were investigated. It was shown that the reaction order with respect to the oxirane, catalyst, and reactive groups of acid is equal to 0.5, 0.5, and 1.5, respectively. The mechanism of this reaction was proposed. The first elementary reaction step was the formation of an adduct of trithiocyanuric acid with TEA with a molar ratio of 1 : 1. This adduct reacted with oxirane and hence activated it for a reaction with —SH groups. The addition of —SH groups to oxiranes was very fast compared to the reaction of the hydroxyalkyl group with oxiranes, which led to subsequent polyetherols.

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