

Kinetics of Sulfur-Free Thiuram Vulcanization

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Synopsis

Sulfur-free thiuram vulcanization has been investigated at temperatures from 160° to 190°C over 0.5 to 600 min. Continuous measurements in a VUREMO curemeter were used to estimate the extent of crosslinking, which was plotted against cure time. Simultaneously the values of the network chain density were calculated from swelling measurements on the vulcanizates. The cure curves show clearly an induction period (t_i), then fast crosslinking, a partial degradation, a "long-time" crosslinking, and finally a slow, limited degradation. Apart from the induction period, the kinetic graphs are satisfactory represented by a rate equation assuming three independent first-order reactions: fast crosslinking, degradation, and slow crosslinking. The rate equation contains seven kinetic parameters. Over the temperature range studied, there is no difference between the values of activation energy for fast crosslinking, for degradation, for slow crosslinking, and for t_i^{-1} . Due to the presence of thiourea, the values of the induction period, the rate constant, and the extent of slow crosslinking are decreased. Simultaneously the activation energies calculated from degradation and slow crosslinking are significantly increased. On the basis of the above results, the mechanism of the sulfur-free thiuram vulcanization, in which ionic and radical reactions take place, is discussed.

INTRODUCTION

Reviews devoted to the kinetics and mechanism of vulcanization have appeared recently.^{1,2} Using the kinetic approach, observation may be made on the rates of disappearance and creation of chemical species, as in the work of Scheele and co-workers^{1,3} or of changes in physical properties of the vulcanizate, as in the methods of Gee and Morrell,⁴ Dogadkin et al.,⁵ Ellis and Welding,^{6,7} and Russell et al.⁸

The majority of these papers are related to the accelerated vulcanization of elastomers by sulfur. A very interesting field is also the vulcanization of unsaturated rubbers by sulfur donors, e.g., tetraalkylthiuram disulfides, in the absence of elemental sulfur.⁹ In our recent study about the influence of the concentration of tetramethylthiuram disulfide (TMTD) on the sulfur-free vulcanization of natural and butadiene rubbers,¹⁰ we found that the shape of the cure curve at high concentrations of TMTD (about 50 phr) and at high cure temperatures (about 180°C) resembles the curve which Russell and co-workers⁸ had obtained for the vulcanization of thiazole-accelerated natural rubber-sulfur compounds. This effect has not been published previously, so far as we know.

The present work shows new features in sulfur-free thiuram vulcanization which include a first-order "longtime" crosslinking reaction. The cure curves have been characterized by seven kinetic parameters. The temperature and concentration dependence of these and the effect of thiourea have been examined.

EXPERIMENTAL

Compounding

The mix formulation was rubber, 100.0 parts, zinc oxide, 5.0 phr, thiourea, 0.0 and 1.0 phr, tetramethylthiuram disulfide, variable. The rubbers used were natural rubber (pale crepe) and *cis*-1,4-polybutadiene (Europren *cis*, exported by Anic, Milan, Italy).

Mixing was by master batch technique on a laboratory mill with 600 × 300-mm rolls at 50°C. Mooney viscosity of natural rubber compounds was 10°ML (1 + 4) at 100°C. This, according to Wolstenholme,¹¹ is equivalent to a number-average molecular weight of 1.2×10^5 . Mooney viscosity of *cis*-1,4-polybutadiene compounds was 30°ML (1 + 4) at 100°C, and their number-average molecular weight, according to Meissner,¹² was also 1.2×10^5 .

Measurement of Cure Curves

The curves reported in the present paper were obtained from continuous measurements of vulcanization on a VUREMO curemeter, type AC-O1 (exported by Metrimpex, Budapest, Hungary).

The VUREMO is an instrument used to measure VULcanization, RELaxation, and MOdulus. It has been completely described in a publication of Bartha et al.¹³ It consists of an oscillating shaft, driving a disk rotor (with diameter 16 mm and thickness 2 mm) in a rubber-filled cylinder cavity (with diameter 20 mm and height 6 mm) through a selected arc of rotation. In the present work, oscillation angle was 0.7°. The thickness of the specimen is 2 mm. The oscillation rate is 2/min. The cavity is heated hydraulically with temperature control in the range of $\pm 0.5^\circ\text{C}$.

Some lag time is involved in heating the specimen of the rubber compound to the intended cure temperature. This must be considered if results at more than one temperature are to be compared. An empirical correction curve is given in Figure 1, which shows the effective time at impressed temperature versus the elapsed time of cure.

The extent of crosslinking was expressed in VUREMO units (torque) and plotted against time of cure.

Measurement of Network Chain Density

The ultimate extent of three vulcanization reactions (fast crosslinking, degradation, and slow crosslinking) was expressed as the network chain density in moles/cm³.

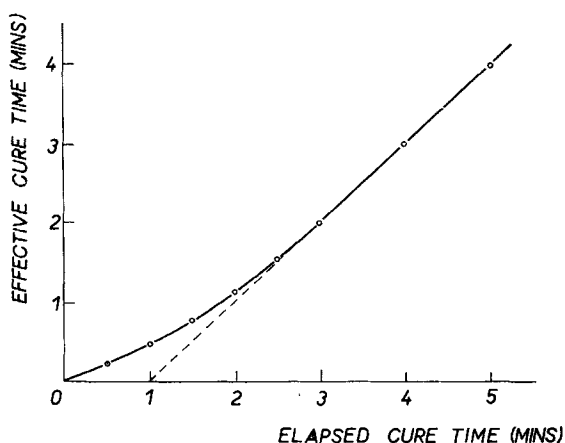


Fig. 1. Correction curve for VUREMO curemeter.

For cure, an electric-heated press was used. The samples (of about 0.2 g) were swollen in toluene at 20°C in separate tubes. Each sample was weighed dry, then swollen in 50 ml toluene for 24 hr, and twice transferred to fresh toluene for a further 24 hr, after which it was dried with filter paper and the swollen weight was measured. The samples were dried at 20°C for seven days and the deswollen weight was measured. The time schedule for mixing, curing, swelling, and deswelling was standardized as far as possible.

The swollen and deswollen weights were used to calculate the volume fraction of rubber, v_r , in the network swollen to equilibrium. For calculation of network chain density, the Flory-Rehner equation¹⁴ was used, with effective values of the *cis*-1,4-polybutadiene-toluene interaction parameter of $0.34 + 0.35 v_r$ published by Meissner.¹²

RESULTS AND DISCUSSION

Influence of Concentration of TMTD on Shape of Cure Curve

When the concentration of TMTD is increased, the rate and the degree of degradation and simultaneously the rate of "long-time" crosslinking also increase. Figures 2 and 3 show that these reactions are faster in *cis*-1,4-polybutadiene than in natural rubber. That is why the cure curve of *cis*-1,4-polybutadiene with 50 phr of TMTD has only four parts: (1) main (fast) crosslinking; (2) partial degradation; (3) long-time crosslinking; and (4) slow limited degradation.

The full line in Figure 4 is a typical graph of the degree of the vulcanization versus log cure time, showing these features better. Figure 4 shows also the ranges characterized previously by different authors.

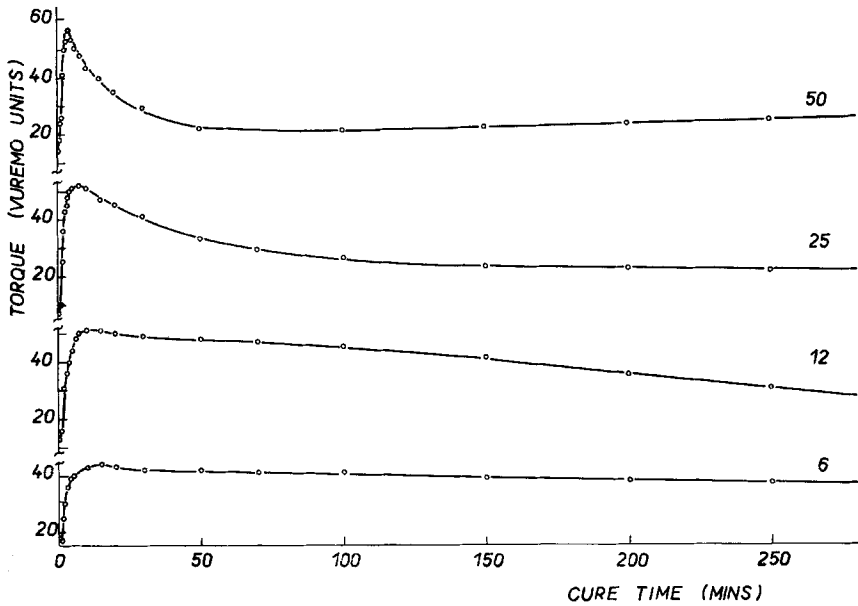


Fig. 2. Influence of concentration of TMTD on the vulcanization of natural rubber at 180°C. Mix formulation: pale crepe 100, ZnO 5, TMTD variable. Numbers on the curves are concentrations of TMTD in phr.

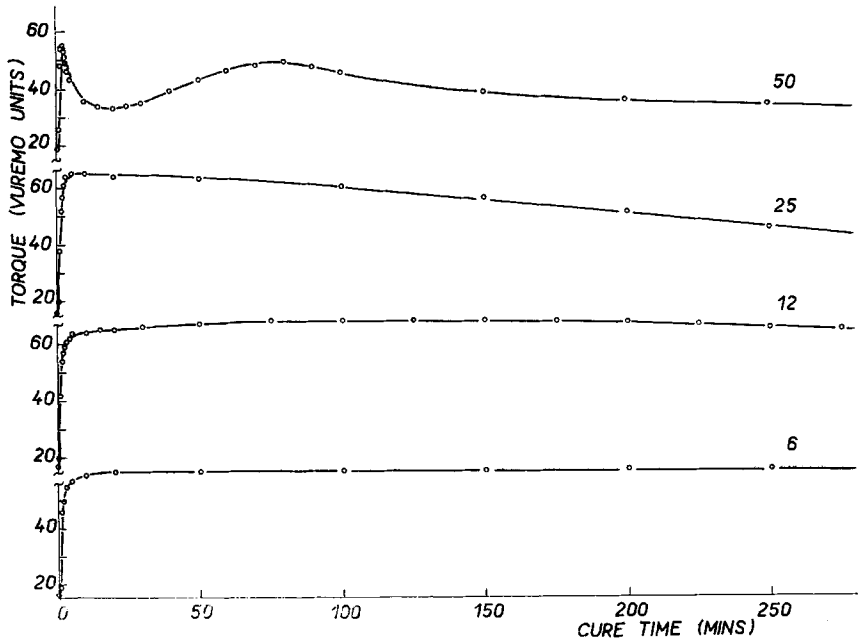


Fig. 3. Influence of concentration of TMTD on the vulcanization of *cis*-1,4-polybutadiene at 180°C. Mix formulation: Europren *cis* 100, ZnO 5, TMTD variable. Numbers on the curves are concentrations of TMTD in phr.

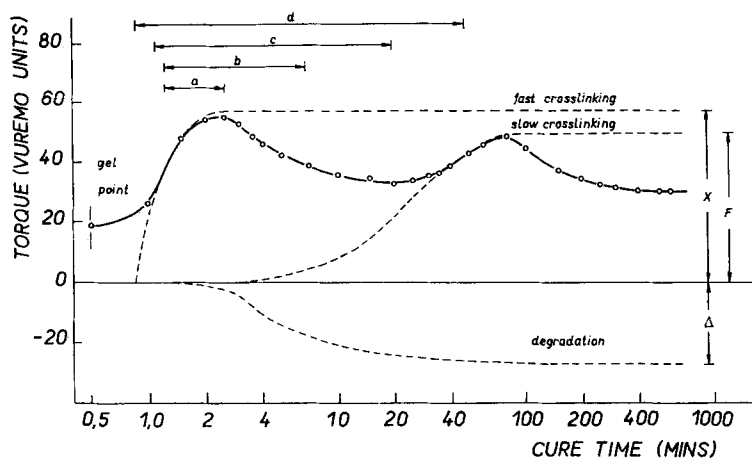


Fig. 4. Kinetic analysis of experimental data of the vulcanization of *cis*-1,4-polybutadiene at 180°C. Mix formulation: Europren *cis* 100, ZnO 5, TMTD 50 (phr); (—) calculated curve fitted to data; (---) estimated contributions from individual reactions; (↔) range previously characterized by (a) Gee and Morrell, (b) Dogadkin et al.,⁵ (c) Ellis and Welding,^{6,7} (d) Russell and co-workers.⁸

Kinetic Analysis

The cure curves have been analyzed by treating them as the sum of three independent first-order reactions, following an induction period, t_i :

$$x = X(1 - e^{-k_i t})$$

$$\delta = \Delta(1 - e^{-k_\delta t})$$

$$f = F(1 - e^{-k_f t})$$

where the contributions to the extent of crosslinking at any time t are given by x , δ , and f , and k_i , k_δ , and k_f , are the respective rate constants. The seven parameters are described in Table I. They were determined by graphic fitting of master curves to the data. This method is detailed in a publication of Redding and Smith.¹⁵ The evidence for the proposed reaction order $n = 1$ is given in Figure 5, where the logarithm of the extent of the

TABLE I
Definitions of Kinetic Parameters

Reaction	Symbol	Units	Definition
Fast crosslinking	t_i	min	induction period
	k_i	min ⁻¹	rate constant
	X	moles chains/cm ³	ultimate extent
Degradation	k_δ	min ⁻¹	rate constant
	Δ	moles chains/cm ³	ultimate extent
Slow crosslinking	k_f	min ⁻¹	rate constant
	F	moles chains/cm ³	ultimate extent

vulcanization reactions is plotted against cure time. Figure 4 shows a typical result. In this graph, the full line represents the sum of three constituent curves fitted to the experimental points shown, and it is described by the expression

$$E = X(1 - e^{-k_i t}) + \Delta(1 - e^{-k_\delta t}) + F(1 - e^{-k_f t})$$

where E is the extent of crosslinking at time t , and $t = (\text{"cure time"} - t_i)$.

Concentration and Temperature Dependence of Kinetic Parameters and the Effect of Thiourea

Dependence of the kinetic parameters on the concentration of TMTD for the range from 3 to 50 phr is given in Table II. The maximum values of the rate and the extent of fast crosslinking reaction at concentration 15 phr of TMTD are attributable to the fact that the weight fraction TMTD:ZnO = 15:5 = 3:1 is in accord with the optimal concentration of ZnO, 1 phr in the rubber compound containing 3 phr of TMTD.^{10,16}

Curves 0 in Figures 6 and 7 show these features better. Curve 1 in Figure 6 presents the accelerating action of thiourea on the rate constant k_i , and curve 1 in Figure 7 presents its action on the ultimate extent of fast crosslinking reaction X . The second effect of thiourea is diminished in the presence of other free-radical inhibitors (e.g., phenyl- β -naphthylamine, N-phenyl-N'-isopropyl-*p*-phenylenediamine, or 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol)).¹⁷

Table III gives the values for the seven parameters for vulcanization of *cis*-1,4-polybutadiene by 50 phr of TMTD in the absence and in the presence of 1 phr of thiourea at four curing temperatures. Arrhenius plots of $\log(t_i^{-1})$, $\log k_i$, $\log k_\delta$, and $\log k_f$ versus reciprocal absolute temperature are given in Figures 8 and 9. Activation energy calculated from these is given in Table IV; in the absence of thiourea, its values are practically independent of calculated constants (22 ± 1 kcal/mole).

Due to the presence of thiourea, the values of the induction period and the rate constant and the extent of slow crosslinking are decreased. Simultaneously, the values of the activation energy calculated from $\log k_\delta$ and \log

TABLE II
Concentration Dependence of Kinetic Parameters of Vulcanization of
cis-1,4-Polybutadiene (ZnO 5 phr, TMTD Variable) at 180°C

TMTD, phr	t_i , min	k_i , min ⁻¹	X , (moles/ cm ³) $\times 10^4$	k_δ , min ⁻¹	Δ , moles/ cm ³ $\times 10^4$	k_f , min ⁻¹	F , (moles/ cm ³) $\times 10^4$
3	0.6	0.63	0.73	—	—	—	—
5	0.4	1.26	1.39	—	—	—	—
15	0.3	3.30	1.60	0.002	0.26	—	—
25	0.3	3.21	1.50	0.004	0.29	—	—
35	0.3	3.10	1.32	0.021	0.29	0.010	1.30
50	0.3	3.07	1.02	0.281	0.30	0.068	0.92

TABLE III
 Temperature Dependence of Kinetic Parameters of Vulcanization of *cis*-1,4-Polybutadiene (TMTD 50 phr, ZnO 5 phr)

Thio- urea phr	Cure temp., °C	t_i , min	k_i , min ⁻¹	X_i , (moles/ cm ³) × 10 ⁴	k_b , min ⁻¹	Δ , (moles/ cm ³) × 10 ⁴	k_f , min ⁻¹	F_i , (moles/ cm ³) × 10 ⁴
0	160	0.8	0.95	1.13	0.092	0.34	0.030	0.95
	170	0.6	1.64	1.03	0.167	0.30	0.046	0.93
	180	0.3	3.07	1.02	0.281	0.30	0.068	0.92
1	190	0.2	5.12	0.99	0.535	0.30	0.164	0.90
	160	0.4	0.80	1.13	0.029	0.37	—	—
	170	0.3	2.00	1.09	0.096	0.35	—	—
	180	0.2	3.30	1.07	0.307	0.39	0.022	0.74
	190	0.1	4.60	0.96	0.834	0.35	0.070	0.68

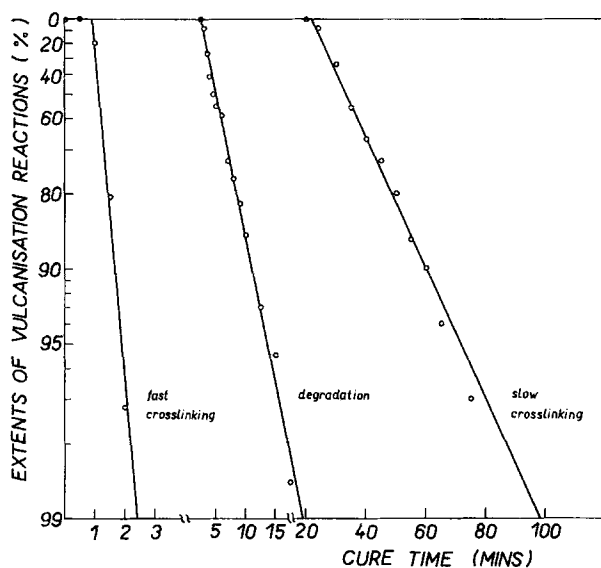


Fig. 5. Increase of extent of vulcanization reactions according to first order in *cis*-1,4-polybutadiene at 180°C. Mix formulation: Europren cis 100, ZnO 5, TMTD 50 (phr).

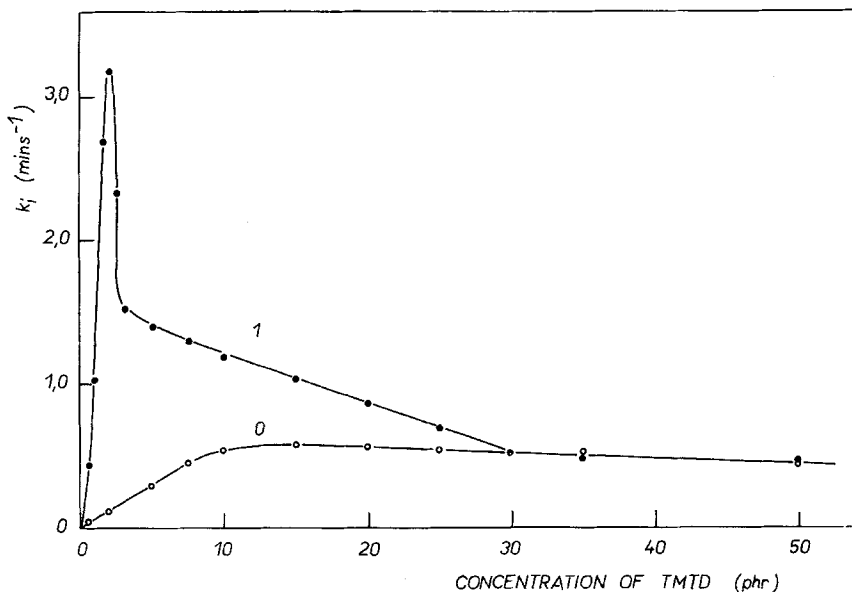


Fig. 6. Influence of concentration of TMTD on the rate constant of fast crosslinking reaction, k_t , and the effect of thiourea (at 145°C). Mix formulation: Europren cis 100, ZnO 5, thiourea 0 and 1, TMTD variable. Numbers on the curves are the concentrations of thiourea in phr.

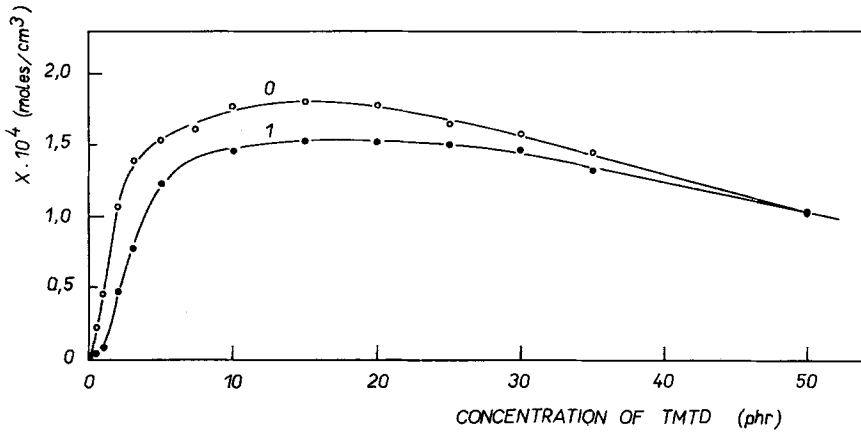


Fig. 7. Influence of concentration of TMTD on the ultimate extent of fast crosslinking reaction, X , and the effect of thiourea (at 145°C). Mix formulation: Europren cis 100, ZnO 5, thiourea 0 and 1, TMTD variable. Numbers on the curves are the concentrations of thiourea in phr.

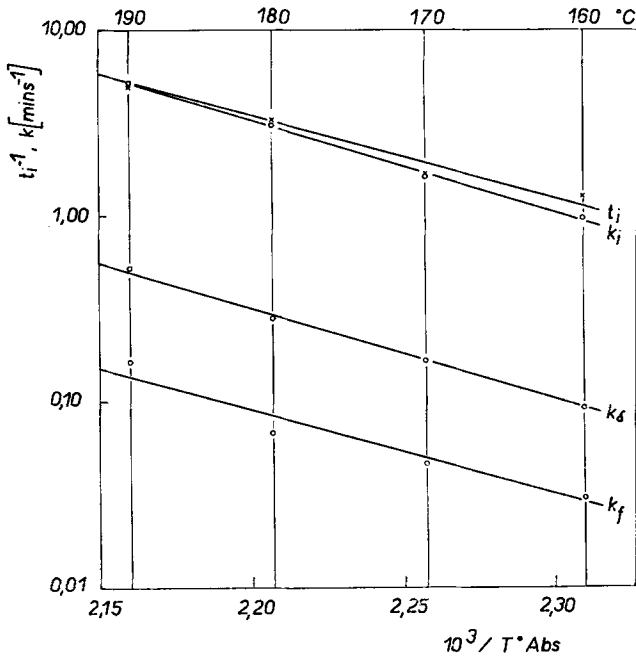


Fig. 8. Effect of temperature on kinetic parameters t_i^{-1} , k_i , k_{δ} , and k_f for vulcanization of *cis*-1,4-polybutadiene in the absence of thiourea. Mix formulation: Europren cis 100 ZnO 5, TMTD 50 (phr).

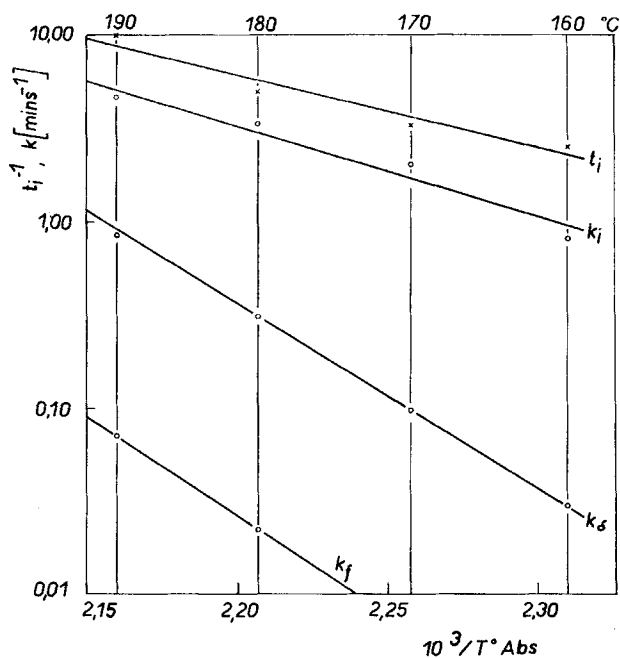


Fig. 9. Effect of temperature on kinetic parameters t_i^{-1} , k_t , k_d , and k_f for vulcanization of *cis*-1,4-polybutadiene in the presence of thiourea. Mix formulation: Europren *cis* 100, ZnO 5, TMTD 50, thiourea 1 (phr).

TABLE IV
Activation Energies (kcal/mole) of vulcanization of *cis*-1,4-Polybutadiene
(TMTD 50 phr, ZnO 5 phr)

Calculated from	Activation energy, kcal/mole (phr)	
	Thiourea = 0	1
(Induction period) ⁻¹	20.5	21.3
Rate constant for fast crosslinking	22.8	22.1
Rate constant for degradation	22.0	44.7
Rate constant for slow crosslinking	20.8	47.9

k_f are twice those calculated from $\log(t_i^{-1})$ and $\log k_t$, which are the same as in the absence of thiourea.

CONCLUSIONS

These results confirm the validity of the mechanism of the sulfur-free thiuram vulcanization proposed previously by us.¹⁸ In the initial steps of vulcanization, characterized by an induction period and fast crosslinking, mainly ionic reactions take place.¹⁹ This is in accord with theories of Bateman and Moore.^{2,20} In the next steps, characterized by degradation and slow crosslinking, mainly radical reactions take place.

Support for this view derives from the influence of thiourea, which is known not only as secondary accelerator of thiuram vulcanization,^{2,20} but also as radical scavenger.²¹ It seems most probable from the results of our recent studies^{10,22} that the retardation effect of thiourea on slow crosslinking is attributable to the action of its oxidation product, formamidine disulfide.

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