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Tetravalent Cerium/Thioglycerol Couple Initiated Polymerization of Methyl Methacrylate

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ABSTRACT

The kinetics of vinyl polymerization of methyl methacrylate initiated by the Ce(IV)/thioglycerol couple were investigated in an aqueous system in the temperature range 5-20°C. The rate of polymerization, the rate of Ce(IV) disappearance, etc. were measured at various concentrations of the monomer, thioglycerol (TG), and ceric ion. The effect of some electrolytes and organic nitrogen compounds, presumed to behave as ideal retarders or inhibitors, has been investigated. The proposed reaction scheme involves initiation by an organic free radical produced by direct interaction of Ce(IV) with the activator (TG) and termination by Ce(IV). Various rate parameters have been evaluated.

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INTRODUCTION

Mercaptans, used as molecular weight modifiers in free radical vinyl polymerization, exert an activating influence on metal and nonmetal ions. The use of mercaptans as components in the redox couple-initiated vinyl polymerization has often been investigated [1-13]. The interaction of these compounds with higher valency transition metal ions to create free radicals seems to be facile. We have reported [14-23] the polymerization of acrylonitrile and methyl methacrylate using Cr(VI), V(V), Mn(III), Mn(IV), and Ce(IV) with thiourea, thioacetamide, thioglycolic acid, and ethanethiol as redox couples. A review of the literature reveals that no report has appeared on the use of thioglycerol as the redox component in the kinetic investigation of vinyl polymerization. Thioglycerol containing both hydroxyl and thiol group seems to be a potential activator for use as the redox component. We have thus investigated the use of thioglycerol as the activator in various metal ion-initiated vinyl polymerizations. The present report on the Ce(IV)/thioglycerol couple-initiated polymerization of methyl methacrylate, is one aspect of our research program.

EXPERIMENTAL

Methyl methacrylate (MMA) (Sisco Chemicals, India) was washed with 5% NaOH to remove the inhibitor, followed by washing with distilled water to remove any traces of alkali. Ceric ammonium sulfate (BDH) and sulfuric acid (18 M, AR) were used. Thioglycerol was purified by distillation under reduced pressure, with the middle fraction being collected. All other reagents were of BDH quality and were used as such.

Water used for the preparation of the solution was purified by distillation thrice over alkaline permanganate and deionized by passage through Biodeminrolit resin (Permutit Co., U.K.). Nitrogen used for the deaeration of the reaction mixture was purified by passage through Fieser's solution, through saturated lead acetate solution, and finally through distilled water containing a little monomer. The Ce(IV) stock solution (0.1 M) was prepared by dissolving 15.81 g of ceric ammonium sulfate in 250 mL of 3 M sulfuric acid. The strength of the stock solution was determined by cerimetry using Ferroin as the indicator.

The polymerization reaction was carried out as reported earlier [17]. After the desired time intervals, the reaction was arrested by adding a known excess of Fe(II) solution. The precipitated polymer was filtered out and dried to constant weight at 60°C. The rate of polymerization (R_p) was determined by gravimetry, and the rate of ceric ion disappearance ($-R_{Ce}$) was determined by cerimetry through an estimation of the excess Fe(II) in the filtrate.

The molecular weights $\overline{M}_v$ of the purified polymers were determined in an Ubbelohde-type suspended level dilution viscometer, using the appropriate Mark-Houwink relationship. Viscosities of the polymer solution in acetone (0.1%) were determined by using the relationship [24]

$$[\eta] = 7.7 \times 10^{-3}\ \overline{M}_v^{\,0.7}\ \text{dL/g}$$

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid at 5 to 20°C in the presence of the redox couple, Ce(IV)/thioglycerol. Time conversion plots at 10°C for various concentrations of thioglycerol (0.0005 to 0.01 M) are shown in Fig. 1. Methyl methacrylate was also polymerized under identical conditions with the Ce(IV)/glycerol couple. The results are presented in Table 1, which shows that thioglycerol is a more powerful activator than glycerol.

The difference in reactivity of the substrates is due to the sulfur atom of the thiol group in the former, which undergoes facile oxidation with respect to the OH group to generate the initiating free radical.

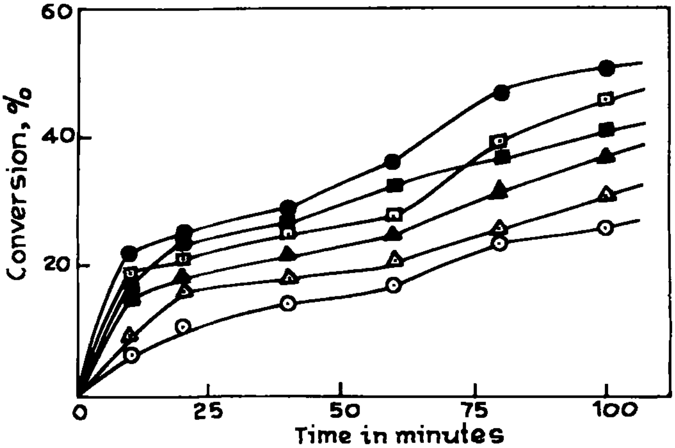


FIG. 1. Variation of conversion % with time: Effect of thioglycerol. [Ce(IV)] = 0.02 M, [H^+] = 0.2 M, [MMA] = 0.09388 M, 10°C. [TG] values: (⊙) 0.0005 M, (△) 0.001 M, (▲) 0.0025 M, (⊡) 0.0035 M, (●) 0.005 M, (■) 0.0075 M.

TABLE 1. Polymerization of Methyl Methacrylate by Ce(IV)/Glycerol and Ce(IV)/Thioglycerol Couples: [Ce(IV)] = 0.02 M, [H^+] = 0.2 M, [MMA] = 0.09388 M, [TG] = 0.005 M, 10°C

Activator	$R_p \times 10^6$, $mL^{-1}\ s^{-1}$
Thioglycerol	4.978
Glycerol	2.765

Rate of Polymerization (R_p)

The rate of polymerization (R_p) increased linearly on increasing the concentration of the monomer (0.047 to 0.3286 M). Plots of R_p vs $[M]^2$ passing through the origin (Fig. 2) and of log R_p vs log [M] with a slope equal to 2 indicate a second-order dependence of the rate on monomer concentration. Further, R_p increased linearly on increasing the concentration of the activator thioglycerol (TG) from 0.0025 to 0.01 M and thereafter decreases. R_p vs [TG] plots pass through the origin (Fig. 3) and plots of log R_p vs log [TG] with a slope equal to unity (Fig. 3) indicate a first-order dependence of the rate on activator concentration. The deviation from linearity of higher [TG] might be due to: 1) a change in the polarity of the medium, 2) chain transfer reactions caused by the mercaptan, and 3) an increase in the rate of oxidation. Similar observations were also made by us in our previous communications [19, 24]. R_p values also increase regularly on increasing the concentration of the ceric ion from 0.0025 to 0.01 M and then decrease. Plots of $1/R_p$ vs [Ce(IV)] (Fig. 4) were linear, with the intercept on the rate axis.

Rate of Ceric Ion Disappearance ($-R_{Ce}$)

The rate of ceric ion disappearance ($-R_{Ce}$) is directly proportional to [Ce(IV)]. Plots of $-R_{Ce}$ vs [Ce(IV)] are linear and pass through the origin (Fig. 4). Under the condition of the reaction studied, the rate is independent of monomer concentration, which indicates that ceric ion is directly involved in the initiation. Further $-R_{Ce}$ increases linearly when the concentration of TG is increased. Plots of the reciprocal of the rate vs $[TG]^{-1}$ did not yield linear plot with an intercept, which

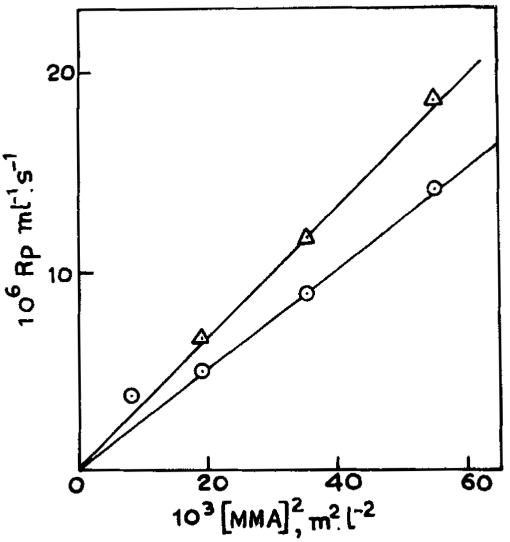


FIG. 2. Variation of rate of polymerization (R_p) with temperature. [Ce(IV)] = 0.02 M, [H^+] = 0.2 M, [TG] = 0.005 M. Temperatures: (⊙) 5°C, (▲) 10°C.

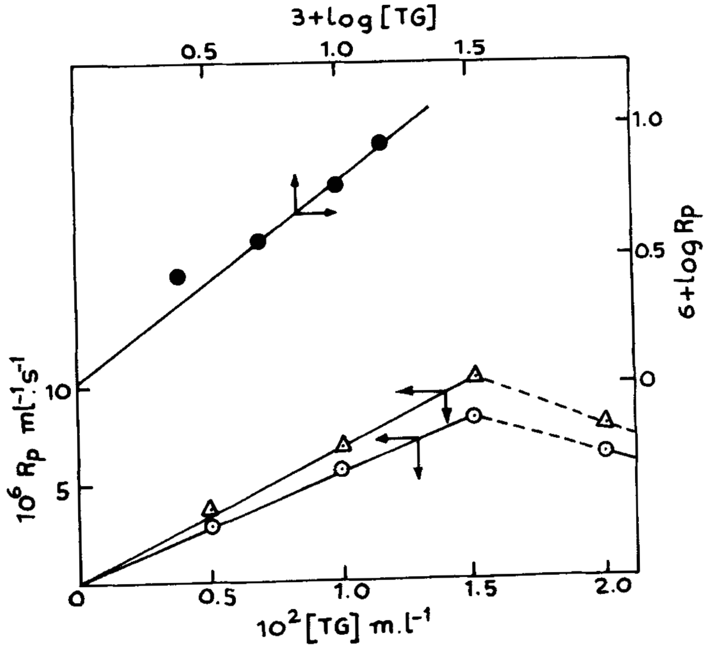


FIG. 3. Variation of rate of polymerization (R_p) with thioglycerol at various temperatures. [Ce(IV)] = 0.02 M, [H^+] = 0.2 M, [MMA] = 0.09388 M. (a) $R_p \times 10^6$ vs [TG] $\times 10^2$: (⊙) 5°C, (▲) 10°C, (b) (6 + log R_p) vs (3 + log [TG]): (●) 5°C.

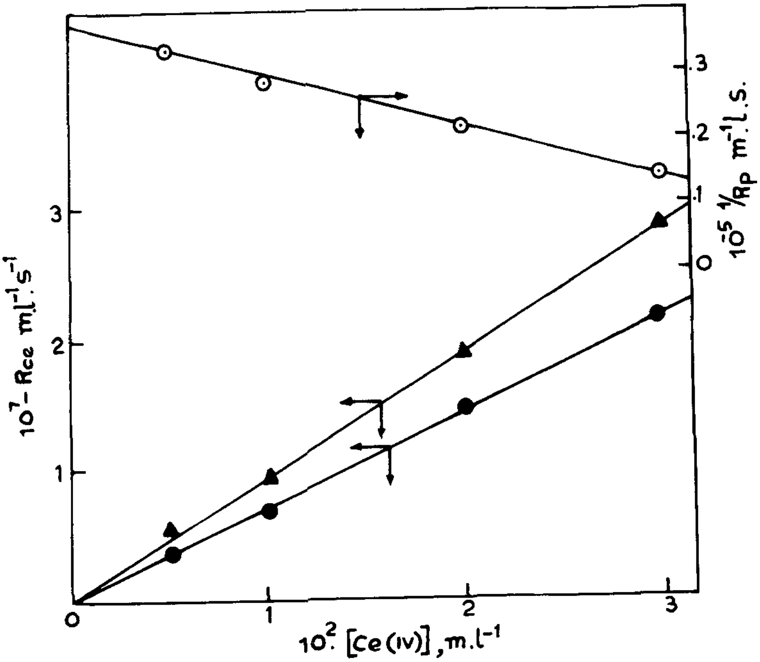


FIG. 4. Variation of rate of polymerization (R_p) and rate of ceric ion disappearance ($-R_{Ce}$) with Ce(IV) at various temperatures. [TG] = 0.005 M, [MMA] = 0.09388 M. (a) $-R_{Ce} \times 10^7$ vs [Ce(IV)] $\times 10^2$: (●) 5°C, (▲) 10°C. (b) $1/R_p \times 10^{-5}$ vs [Ce(IV)] $\times 10^2$: (⊙) 5°C.

indicates that Michaelis-Menten [25] or Lineweaver and Burk [26] kinetics is not applicable. This indicates that no complex formation between Ce(IV) and thioglycerol takes place; rather, direct oxidation results in the formation of the initiating radical. This observation is supported by the work of Guelbault et al. [27] who showed that glycerol fails to form a complex of any type with Ce(IV)-sulfate.

Effect of Acid Concentration

The initial rate of polymerization as well as the maximum conversion were found to be unaffected by increasing the concentration of sulfuric acid from 0.1 to 0.5 M, but at higher concentration of H_2SO_4 there is a slow decrease in the rate. This might be due to a change in the oxidation potential [28, 29] of Ce(IV) with increasing acid concentration.

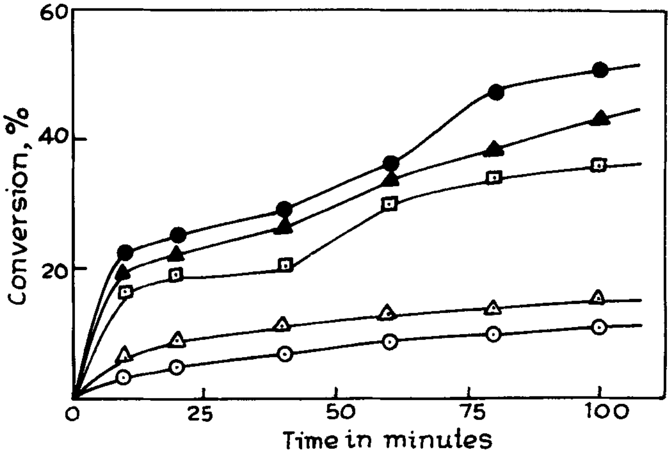


FIG. 5. Variation of conversion % with time: Effect of catalyst concentration. [H^+] = 0.2 M, [MMA] = 0.9388 M, [TG] = 0.005 M, 10°C. (⊙) [Ce(IV)] = 0.0025 M, (△) [Ce(IV)] = 0.005 M, (⊡) [Ce(IV)] = 0.01 M, (●) [Ce(IV)] = 0.02 M, (▲) [Ce(IV)] = 0.035 M.

Effect of Catalyst Concentration

The initial rate of polymerization and the maximum conversion were found to increase with an increase in the concentration of Ce(IV) (0.0025-0.02 M), beyond which the rate decreases progressively (Fig. 5). The rate decrease at higher concentrations of ceric ion might be due to an enhanced rate of linear termination of the polymer chain radicals.

Effect of Added Salts

The addition of a 0.02-M solution of $MnSO_4$, $CuSO_4$, $CoSO_4$, $NiSO_4$, and $FeCl_3$ to the polymerization reaction decreases the initial rate and the maximum conversion to a considerable extent (Fig. 6). Such a behavior of the electrolytes might be due to: 1) complexing of the ceric ion with the sulfate and chloride ions, which decreases the ability of Ce(IV) to interact with the activator to generate free radicals; 2) oxidation of Mn^{2+} and Co^{2+} ions to unstable Mn^{3+} and Co^{3+} ions, which adds to the linear termination; and 3) premature termination of the polymer chains by Cu^{2+} and Fe^{3+} ions. Premature termination of polymer chains by Fe^{3+} and Cu^{2+} has been shown by Bamford et al. [30] in the AIBN-initiated polymerization of vinyl monomers in the

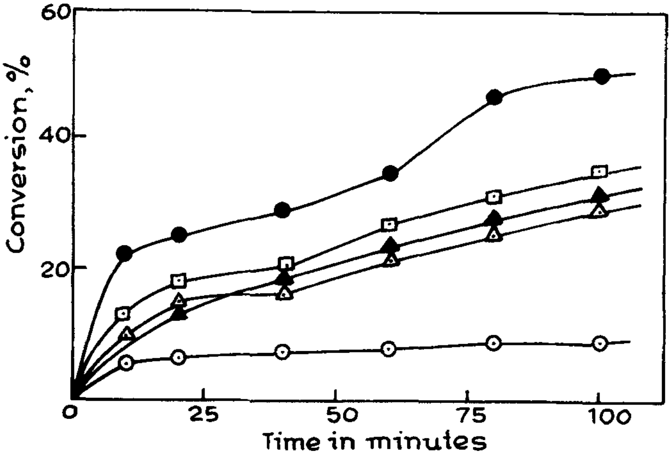


FIG. 6. Variation of conversion % with time: Effect of added electrolytes. [Ce(IV)] = 0.02 M, $[H^+]$ = 0.2 M, [TG] = 0.005 M, [MMA] = 0.09388 M, [electrolyte] = 0.02 M, 10°C. (⊙) $[MnSO_4]$, (△) $[CuSO_4]$, (▣) $[CoSO_4]$, (▲) $[FeCl_3]$, (●) control.

presence of $FeCl_3$ and by Bengough et al. [31] in the AIBN-initiated polymerization of methyl methacrylate in the presence of $CuCl_2$.

Effect of Organic Nitrogen Compounds

Organic nitrogen compounds have been found to exhibit interesting effects on radical polymerization. Addition of a 0.0005-M solution of aniline to the reaction mixture depresses the initial rate and the maximum conversion. With a further increase in the concentration to 0.001 M, the effect becomes more pronounced. At 0.0025 M, no polymer is precipitated (Table 2); rather, a reddish color is produced which persists. This behavior of aniline is due to its oxidation to quinones [32] which are inhibitors of radical polymerization. A similar observation was made by Saha et al. [33] in the ceric-ion-initiated polymerization of acrylonitrile in the presence of N,N-dimethylaniline. Further addition of 0.0005 M pyridine and piperidine separately to the reaction mixture retards the rate, which remains almost constant even though the concentration of the additives is increased from 0.0005 to 0.025 M (Tables 3 and 4). This might be due to the retarding effect of the N-oxides produced by the oxidation of the additives by Ce(IV)-sulfate. N-Oxides are well known to be ideal retarders of vinyl polymerization [34].

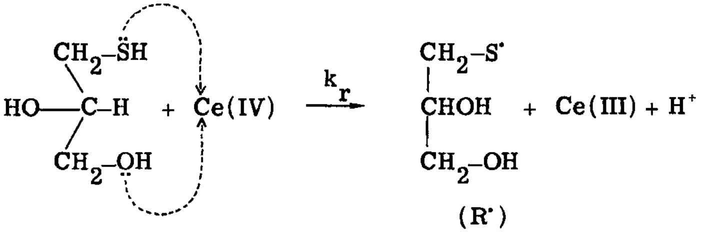
TABLE 2. Effect of Aniline on the Ce(IV)/Thioglycerol Couple Initiated Polymerization of Methyl Methacrylate: [Ce(IV)] = 0.02 M, $[H^+]$ = 0.2 M, [TG] = 0.005 M, [MMA] = 0.09388 M, 10°C

	Conversion, %			
		[An]		
Time, min	Control	0.0005 M	0.001 M	0.0025 M
10	22.34	9.04	5.31	No polymer
20	25.53	12.23	9.57	-
40	29.25	16.49	13.29	-
60	36.70	20.21	15.95	-
80	47.34	22.87	18.93	-
100	50.53	25.53	21.82	-

Reaction Mechanism and Rate Law

Polymerization of methyl methacrylate in aqueous medium, initiated by the Ce(IV)/thioglycerol couple, shows features characteristic of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer in the aqueous phase.

Based on the proportionalities obtained between the measurable parameters and variables, a reaction scheme involving initiation by the organic free radical produced by the interaction of Ce(IV) with thioglycerol and termination by ceric ion is suggested:



(1)

Initiation:

$$R^\bullet + M \xrightarrow{k_i} R\text{–}M_1^\bullet \qquad (2)$$

TABLE 3. Effect of Pyridine on the Ce(IV)/Thioglycerol Couple-Initiated Polymerization of Methyl Methacrylate: [Ce(IV)] = 0.02 M, $[H^+]$ = 0.2 M, [TG] = 0.005 M, [MMA] = 0.09388 M, 10°C

	Conversion, %						
		[Py]					
Time, min	Control	0.0005 M	0.001 M	0.0025 M	0.005 M	0.015 M	0.025 M
10	22.34	11.96	9.04	9.04	8.59	8.95	7.99
20	25.53	18.61	18.35	17.48	15.95	15.42	15.21
40	29.25	22.87	21.77	20.21	20.00	19.6	17.9
60	36.70	34.57	32.97	29.78	29.25	28.92	27.58
80	47.34	39.36	37.23	36.96	34.57	34.01	29.99
100	50.53	45.21	42.55	41.48	41.01	39.96	39.36

TABLE 4. Effect of Piperidine on the Ce(IV)/Thioglycerol Couple-Initiated Polymerization of Methyl Methacrylate: [Ce(IV)] = 0.02 M, [H$^+$] = 0.2 M, [TG] = 0.005 M, [MMA] = 0.09388 M, 10°C

	Conversion, %						
		[Pip]					
Time, min	Control	0.0005 M	0.001 M	0.0025 M	0.005 M	0.015 M	0.025 M
10	22.34	15.42	13.29	12.70	11.95	9.04	7.97
20	25.53	17.01	17.95	18.74	15.42	18.01	14.98
40	29.25	21.80	21.27	23.21	19.68	18.61	17.59
60	36.70	35.10	34.04	32.01	30.85	29.95	27.12
80	47.34	41.48	39.84	38.30	36.17	34.57	35.00
100	50.53	46.27	43.61	43.10	41.84	39.80	38.92

Propagation:

$$\begin{array}{l} R\text{–}M_1^{\bullet} + M \xrightarrow{k_p} R\text{–}M_2^{\bullet} \\ \vdots \\ R\text{–}M_{n-1}^{\bullet} + M \longrightarrow R\text{–}M_n^{\bullet} \end{array} \tag{3}$$

Termination:

$$R\text{–}M_n^{\bullet} + Ce(IV) \xrightarrow{k_t} \text{polymer} + Ce(III) + H^{+} \tag{4}$$

Oxidation:

$$R^{\bullet} + Ce(IV) \xrightarrow{k_0} \text{oxidation products} \tag{5}$$

By applying the steady-state principle to the primary radical $R^{\bullet}$ and the growing polymer radical $R\text{–}M_n^{\bullet}$, and making the usual assumption that the radical reactivity is independent of radical size, we obtain the following rate expressions:

$$R_p = \frac{k_r k_i k_p [TG][M]^2}{k_t(k_i[M] + k_0[Ce(IV)])} \tag{6}$$

The rate of ceric ion disappearance, $-R_{Ce}$, is given by

$$-R_{Ce} = 2k_r[Ce(IV)][TG] \tag{7}$$

The chain length is given by

$$\bar{\nu} = \frac{k_p[M]}{k_t[Ce(IV)]} \tag{8}$$

The mutual and primary radical terminations were discarded because the expressions for R_p and $-R_{Ce}$ involved proportionalities which were not experimentally realized.

Evaluation of Rate Constants

The value of k_r was obtained by plotting $-R_{Ce}$ vs [Ce(IV)] or [TG]. The values of k_p/k_t and k_0/k_i were obtained from Eq. (6), which on rearrangement yields

$$\frac{1}{R_p} = \frac{k_t}{k_p k_r [TG][M]} + \frac{k_t k_0 [Ce(IV)]}{k_p k_i k_r [M]^2 [TG]} \qquad (9)$$

Plots of $1/R_p$ vs [Ce(IV)] according to Eq. (9) are linear with their intercepts on the rate axis (Fig. 4). From the intercepts and slopes of the plots, the values of k_p/k_t and k_0/k_i have been calculated by using the value of k_r (Table 5).

TABLE 5. Values of Rate Parameters for the Polymerization of Methyl Methacrylate Initiated by the Ce(IV)/Thioglycerol Couple at 5°C

Temperature, °C	$10^3\ k_r$ L/mol·s	$10^{-2}\ k_p/k_t$	$10^{-3}\ k_0/k_i$
5	6.964	0.2186	1.032

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