Kinetics and mechanisms of the redox reactions of the thallium(III) ions with crotonaldehyde and methacrolein

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The stoichiometry, kinetics, and mechanisms of the redox reactions of thallium(III) sulfate with crotonaldehyde and methacrolein in aqueous solution of sulfuric acid or binary water—dioxan mixture have been studied. A molecule of crotonaldehyde or methacrolein is oxidized by the Tl(III) ions in two consecutive one-electron steps to give 2,3-dihydroxybutyraldehyde or 2,3-dihydroxyisobutyraldehyde. The redox reaction is governed by the rate equation $-d[Tl(III)]/dt = k[Tl(III)]^n[S]$ where $n = 0-2$. The zero reaction order with respect to the Tl(III) ions may be explained by slow enolization of the hydrated crotonaldehyde and methacrolein which is the rate-determining step and precedes the proper redox step.

Была изучена стехиометрия, кинетика и механизмы окислительно-восстановительных реакций сульфата таллия(III) с кротоновым альдегидом и метакролеином в водном растворе серной кислоты или в бинарной смеси вода–диоксан. Молекулы кротонового альдегида и метакролеина окисляются ионами Tl(III) в двух последовательных одноэлектронных ступенях до 2,3-дигидроксибутиральдегида и 2,3-дигидроксиизобутиральдегида. Реакции восстановления отвечает уравнение скорости $-d[Tl(III)]/dt = k[Tl(III)]^n[S]$, где $n = 0-2$. Нулевой порядок реакции по ионам таллия объясняется медленной энолизацией гидратированного кротонового альдегида и метакролеина, которая предшествует, как ступень, определяющая скорость, ступени самого окисления.

The thallium(III) ions in aqueous solutions are rather strong oxidizing agents, the standard redox potential of the Tl(III)—Tl(I) system at 25°C being 1.25 V [1, 2]. However, it significantly depends on the pH value and the presence of complex-forming ions [3]. The relatively strong oxidation effects of the Tl(III) ions are also employed in oxidations of unsaturated organic substances, *e.g.* olefins, carbonyls, *etc.* [4—6]. In particular, the weight of the papers published by *Henry* [7—9] should be emphasized. The oxidation of alkenes in aqueous solutions affords two characteristic types of products, *i.e.* carbonyl compounds (aldehydes and ketones) and vicinal diols. This reaction is to be described by the following reaction scheme

$$Tl^{3+} + CH_2{=}CHR + H_2O \rightarrow H^+ + [TlCH_2CH(OH)R]^{2+}$$

$$[TlCH_2CH(OH)R]^{2+} \xrightarrow[H_2O]{} \begin{array}{l} CH_3COR + Tl^+ + H^+ \\ CH_2(OH)CH(OH)R + Tl^+ + H^+ \end{array} \qquad (A)$$
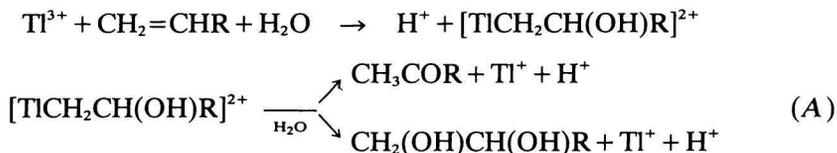
Some α,β-unsaturated carbonyl compounds, $Ar{-}\overset{\cdot}{C}H{=}CH{-}Br$ and $CH_2{=}CH{-}CN$, are not subject to oxidation by the Tl(III) ions [4, 10]. Sometimes, the oxidation can be performed at a higher temperature by extending the reaction time which, however, gives rise to a mixture consisting of hardly definable products [11].

Watanabe et al. [12, 13] studied the oxidation of unsaturated aliphatic aldehydes $R^1CH{=}CR^2CHO$ (R^1, $R^2 = H$, Me) by the Tl(III) ions in aqueous solution of acetic acid or alcohols (R^3OH, $R^3 = C_1{-}C_3$ alkyl). On the basis of this study, they have revealed that the oxidation does not take place on olefinic carbon atoms but the carbonyl group is oxidized to carbonyl group and the compound $R^1CH{=}CR^2CO_2H$ or $R^1CH{=}CR^2CO_2R^3$ arises. Since the acids or esters formed are monomers of different polymers, we have taken a resolution to investigate these reactions kinetically in more detail in order to elucidate their mechanism [14]. The kinetics of oxidation of crotonaldehyde and methacrolein by the Tl(III) ions is also studied in this paper from the view-point of an extensively conceived research into the influence of binary mixtures on kinetics and mechanism of redox reactions.

Experimental

Kinetics

The kinetics of oxidation of crotonaldehyde and methacrolein by Tl(III) sulfate in aqueous solution of sulfuric acid was studied polarographically by recording the time dependence of the limiting diffusion current of cathodic wave of the Tl(III) ions at the potential of 0 V against the potential of the 1 M mercurosulfate electrode. A vibrating platinum electrode with the frequency of 50 Hz (12 mm length and 0.5 mm width) was used as an indication electrode. The measurements were carried out on a polarograph OH 102 (Radelkis, Budapest). A temperature-controlled Kalousek vessel served as electrolytic vessel. The temperature was held constant by means of a thermostat U 10 (Medinger, Dresden) ($\pm 0.05°C$).

Chemicals

The solution of Tl(III) sulfate was prepared by electrochemical oxidation of 10^{-2} M solution of Tl_2SO_4 (200 ml) (anal. grade chemical, Lachema, Brno) in 1 M or 0.1 M-H_2SO_4 (anal. grade chemical, Lachema, Brno) in an electrolyzer of the volume of 250 ml at room

temperature. This electrochemical oxidation was performed by means of the Winkler electrodes the cathodic and anodic space of which was separated by a fritted glass disc S 4. The voltage used was equal to 2.0 V, the solution was electromagnetically stirred and the duration of electrolysis was 4 or 5 h. Thus the 8.1×10^{-3} M solution of $Tl_2(SO_4)_3$ in 1 M-H_2SO_4 or 1.5×10^{-3} M solution of $Tl_2(SO_4)_3$ in 0.1 M-H_2SO_4 was obtained. The concentration of the Tl(III) ions was determined by titrating the iodine liberated in the reaction between the Tl(III) ions and KI with a standard solution of $Na_2S_2O_3$ [15].

Crotonaldehyde (pure, Fluka AG, Buchs SG) was distilled in a Vigreux column in nitrogen atmosphere. The fraction with the boiling point of 104—105°C was collected. Methacrolein (pure, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) was distilled in a Vigreux column in nitrogen atmosphere. The fraction with the boiling point of 68—69°C was collected. The substances were preserved in nitrogen atmosphere in a refrigerator [16]. The preparation of the solutions of crotonaldehyde and methacrolein and the manipulation of them as well as the measurements themselves were carried out in nitrogen atmosphere. No solution older than 24 h after distillation was used.

Redistilled water was used for preparing all solutions. Other chemicals and solvents used were anal. grade chemicals (Labora, Brno). The stoichiometry of reactions was determined by polarometric titration.

Results

The redox reaction of the Tl(III) ions with crotonaldehyde or methacrolein proceeds in 0.1 M sulfuric acid at 17.5°C as a zero-order reaction with respect to the Tl(III) ions for 7.5×10^{-4} M-$Tl_2(SO_4)_3$ in the 1.5×10^{-2}—6.5×10^{-2} M concentration region of crotonaldehyde and in the 5.5×10^{-3}—6.5×10^{-2} M concentration region of methacrolein. At lower concentrations of the substrate, the partial reaction order grows from the value of $n_{Tl(III)} = 0$ to the value $n_{Tl(III)} = 1$—2 (Table 1).

For the above concentration regions of crotonaldehyde and methacrolein the equation of the reaction rate may be expressed as follows

$$-d[Tl(III)]/dt = k[Tl(III)]^0[S] = k[S] \qquad (1)$$

where $[S]$ is the concentration of substrate, *i.e.* crotonaldehyde or methacrolein. For the measured value of the limiting diffusion current, it holds

$$I = \varkappa[Tl(III)] \qquad (2)$$

and thus

$$-\frac{dI}{dt} = \varkappa k[S] = k^*[S] \qquad (3)$$

or

$$I = -k^*[S]t + I_0 \qquad (4)$$

Table 1

Reaction order with respect to Tl(III) and with respect to substrates
7.5×10^{-4} M-Tl$_2$(SO$_4$)$_3$; 0.1 M-H$_2$SO$_4$; $t = 17.5°C$

Concentration of crotonaldehyde mol dm^{-3}	Reaction order with respect to Tl(III)	Reaction order with respect to substrate	Rate constant
6.5×10^{-2}	0	1	
5.5×10^{-2}	0	1	
4.5×10^{-2}	0	1	
3.5×10^{-2}	0	1	$k = 1.09 \times 10^{-3}$ s^{-1}
2.5×10^{-2}	0	1	
1.5×10^{-2}	0	1	
7.5×10^{-3}	1	1	
5.5×10^{-3}	1	1	$k' = 0.58$ dm^3 mol^{-1} s^{-1}
2.5×10^{-3}	1	1	
1.5×10^{-3}	2	1	$k'' = 473.3$ dm^6 mol^{-2} s^{-1}

Concentration of methacrolein mol dm^{-3}	Reaction order with respect to Tl(III)	Reaction order with respect to substrate	Rate constant
6.5×10^{-2}	0	1	
5.5×10^{-2}	0	1	
4.5×10^{-2}	0	1	
3.5×10^{-2}	0	1	
2.5×10^{-2}	0	1	$k = 3.3 \times 10^{-5}$ s^{-1}
1.5×10^{-2}	0	1	
7.5×10^{-3}	0	1	
5.5×10^{-3}	0	1	
2.5×10^{-3}	1	1	$k' = 1.5 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}
1.5×10^{-3}	2	1	$k'' = 60$ dm^6 mol^{-2} s^{-1}

The measured dependence of the limiting diffusion current on time is really linear and the value of the rate constant k may be determined from the slope of the graphical representation of this dependence.

Provided the concentration of crotonaldehyde is lower than 1.5×10^{-2} M and that of methacrolein is lower than 5.5×10^{-3} M, the value of n varies between 1 and 2 according to the concentration of the substrate (Table 1).

The value of the measured rate constant is independent of ionic strength and even does not change with concentration of the HSO$_4^-$ ions. The dependence of the rate constant k on concentration of the H$_3$O$^+$ ions can be expressed by the following equation

$$k = k_0 + k_{H_3O^+}[H_3O^+] \qquad (5)$$

The values $k_0 = 3.28 \times 10^{-2}\,\text{s}^{-1}$ and $k_{\text{H}_3\text{O}^+} = 2.28 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ valid for crotonaldehyde and $k_0 = 2.33 \times 10^{-5}\,\text{s}^{-1}$ and $k_{\text{H}_3\text{O}^+} = 1.1 \times 10^{-4}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ valid for methacrolein were found by the method of least squares.

In order to ascertain that the investigated reaction follows the radical mechanism, we studied the effect of a monomer added (acrylonitrile) on reaction rate. Thus we observed a decrease in reaction rate. The value of the experimental rate constant decreased by 6% for crotonaldehyde (at 1.1×10^{-1} M concentration of acrylonitrile) and by 16% for methacrolein (at 1.1×10^{-1} M concentration of acrylonitrile).

Particular attention was paid to the influence of the binary water–dioxan mixture on experimental rate constant. The results of kinetic measurements are given in Table 2. They may be interpreted by plotting $\log k$ against the mole fraction of dioxan or the reciprocal value of dielectric constant (Fig. 1). On the basis of the Eyring equation, we determined the pertinent activation parameters,

Table 2

Variation of rate constant with temperature in the water–dioxan mixture
7.5×10^{-4} M-Tl$_2$(SO$_4$)$_3$; 0.1 M-H$_2$SO$_4$

$t/°C$	x	K $k \times 10^4\,\text{s}^{-1}$	M $k \times 10^5\,\text{s}^{-1}$
17.5	0	9.3	3.3
25	0	12.0	6.3
30	0	14.3	10.4
35	0	16.7	15.8
17.5	0.039	6.9	2.7
25	0.039	8.4	4.5
30	0.039	9.8	6.5
35	0.039	11.5	8.5
17.5	0.063	5.7	2.4
25	0.063	7.0	3.6
30	0.063	8.4	5.0
35	0.063	9.6	6.5
17.5	0.094	4.7	2.1
25	0.094	5.5	2.7
30	0.094	6.5	3.8
35	0.094	8.1	5.4
17.5	0.174	3.8	1.5
25	0.174	4.2	1.9
30	0.174	4.8	2.5
35	0.174	6.0	2.8

K — crotonaldehyde, M — methacrolein, x — mole fraction of dioxan.
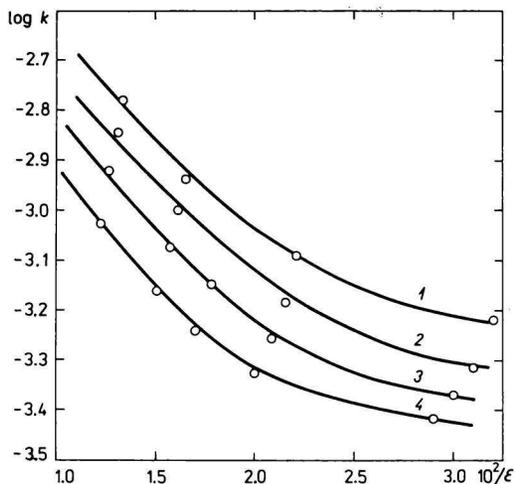
Fig. 1. Variation of the logarithm of rate constant of the redox reaction of the Tl(III) ions with crotonaldehyde with the reciprocal value of dielectric constant in the water−dioxan mixture. Temperatures: *1.* 35°C; *2.* 30°C; *3.* 25°C; *4.* 17.5°C.

Table 3

Activation parameters in the water−dioxan mixture
7.5×10^{-4} M-Tl$_2$(SO$_4$)$_3$; 0.1 M-H$_2$SO$_4$

x	ΔH^+, kJ mol^{-1}		ΔS^+, J K^{-1} mol^{-1}	
	K	M	K	M
0	22.2	64.5	−226	−108
0.039	19.3	46.1	−238	−173
0.063	19.9	39.8	−238	−195
0.094	20.3	37.1	−238	−206
0.174	15.7	24.5	−256	−252

K — crotonaldehyde, M — methacrolein, x — mole fraction of dioxan.

i.e. activation enthalpy ΔH^+ and activation entropy ΔS^+ (Table 3) by the method of least squares.

Discussion

The characteristic feature of the kinetics of oxidation of crotonaldehyde and methacrolein by the Tl(III) ions is a change in the partial reaction order with respect to concentration of the Tl(III) ions in the interval $n_{Tl(III)} = 0—2$. The zero reaction order is observed at the concentration ratio of substrate to the Tl(III) ions

$c_S : c_{Tl(III)} > 3$ for methacrolein and $c_S : c_{Tl(III)} > 10$ for crotonaldehyde. The zero reaction order was also observed in the oxidation of acrolein by the Tl(III) ions [14] as well as in the oxidation of unsaturated aldehydes by the Mn(III) ions [17].

That fact may be explained as follows. The unsaturated aldehyde, for instance crotonaldehyde, is subject to the acid-catalyzed hydration in aqueous solution of sulfuric acid to give the hydrated enol form (E) which is in equilibrium with the corresponding keto form (K)

$$CH_3-CH=CH-C{\overset{O}{\underset{H}{}}} + H^+ \rightleftarrows CH_3-CH=CH-C{\overset{\overset{+}{O}H}{\underset{H}{}}} \qquad (B)$$

$$CH_3-CH=CH-C{\overset{\overset{+}{O}-H}{\underset{H}{}}} \rightleftarrows \qquad (C)$$

$$\rightleftarrows CH_3-CH=CH-\overset{+}{C}H-OH \rightleftarrows CH_3-\overset{+}{C}H-CH=CH-OH$$

$$CH_3-\overset{+}{C}H-CH=CH-OH + H_2O \rightleftarrows CH_3-\underset{\underset{OH}{|}}{CH}-CH=CH-OH + H^+ \quad (D)$$

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH=CH-OH \underset{k_-}{\overset{k_+}{\rightleftarrows}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-C{\overset{O}{\underset{H}{}}} \qquad (E)$$

$$\text{(E)} \qquad\qquad\qquad \text{(K)}$$
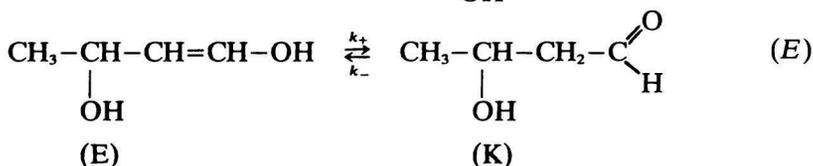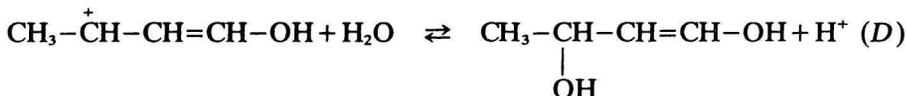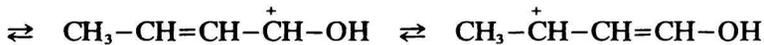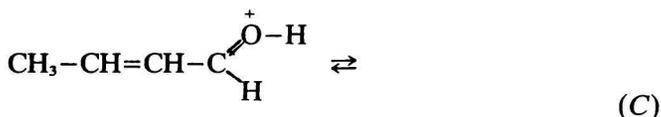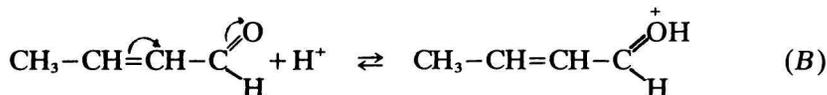
In the presence of the Tl(III) ions, an oxidation of the hydrated enol form takes place in the solution

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH=CH-OH + Tl^{3+} \overset{k^1}{\rightarrow} \left[CH_3-\underset{\underset{OH}{|}}{CH}-CH{\overset{|}{\underset{Tl}{}}}CH-OH \right]^{3+} \xrightarrow{2H_2O}$$

$$\xrightarrow{2H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C{\overset{OH}{\underset{H}{\overset{}{-}OH}}} + Tl^+ + 2H^+ \qquad (F)$$

$$\downarrow{-H_2O}$$

$$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C{\overset{O}{\underset{H}{}}}$$
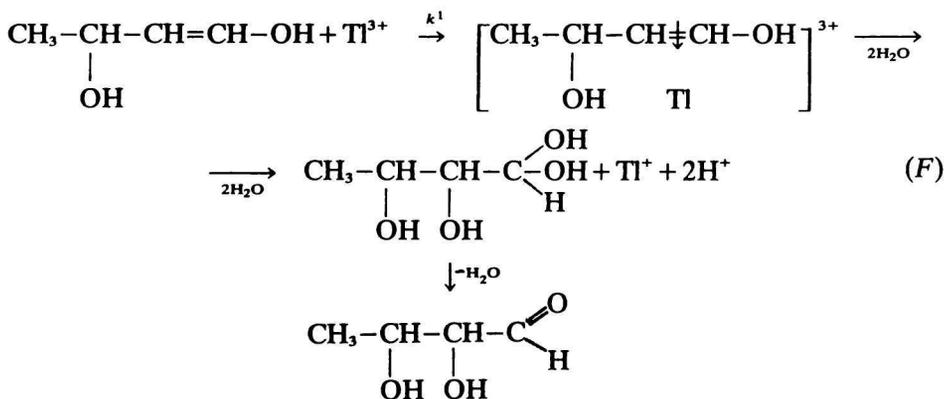
Redox reaction (F) obeys the rate equation

$$-d[Tl(III)]/dt = k^1[Tl(III)][E] \qquad (6)$$

The observed partial zero reaction order may be explained on the assumption that the rapid redox step (F) is preceded by a slow enolization which is likely to be the rate-determining step. In the major part of the reaction progress we may assume a steady state obeying the equation

$$\frac{d[E]}{dt} = 0 \tag{7}$$

Then it holds

$$k_-[K] - k^1[E][Tl(III)] = 0 \tag{8}$$

and thus

$$[E]_s = k_-[K]/k^1[Tl(III)] \tag{9}$$

If we insert stationary concentration (9) for the concentration of the enol form into rate eqn (6), we obtain

$$\frac{-d[Tl(III)]}{dt} = k_-[K] \tag{10}$$

Eqn (10) shows that the reaction is of the zero order with respect to the Tl(III) ions and the product $k_-[K]$ is a constant provided the substrate is present in sufficient excess.

At the concentration ratio of substrate to the Tl(III) ions $c_s : c_{Tl(III)} = 1$ (for crotonaldehyde and methacrolein as well), we observe that the reaction order with respect to the Tl(III) ions is equal to two. In this case, the concentration of substrate is no more sufficient for establishment of a steady state and the oxidation of substrate, e.g. crotonaldehyde, must proceed in two consecutive steps

$$CH_3-CH-CH=C\overset{OH}{\underset{H}{<}} \quad Tl^{3+} + H_2O \overset{k_1}{\rightarrow}$$
$$\underset{OH}{|}$$

$$CH_3-CH-\overset{OH}{\overset{|}{CH}}-C\overset{OH}{\underset{H}{<}}$$
$$\underset{OH}{|} \qquad \qquad + Tl^{2+} + H^+ \tag{G}$$

$$CH_3-CH-CH-C\overset{OH}{\underset{OH}{-H}}$$
$$\underset{OH}{|}$$

(R)

$$R + Tl^{3+} + H_2O \xrightarrow{k_2} \left\{ \begin{array}{l} \underset{OH}{\overset{OH}{CH_3-CH-CH-C\overset{OH}{\underset{OH}{-}}H}} \\[2em] \underset{OH\ OH}{CH_3-CH-CH-C\overset{OH}{\underset{OH}{-}}H} \end{array} \right. + Tl^{2+} + H^+ \qquad (H)$$

$$\downarrow^{-H_2O}$$

$$\underset{OH\ OH}{CH_3-CH-CH-C\overset{\diagup O}{\diagdown H}}$$

$$2Tl^{2+} \rightarrow Tl^+ + Tl^{3+} \qquad (I)$$
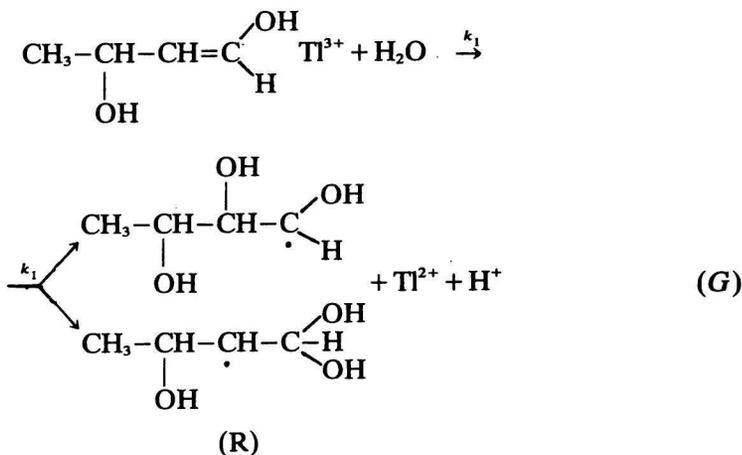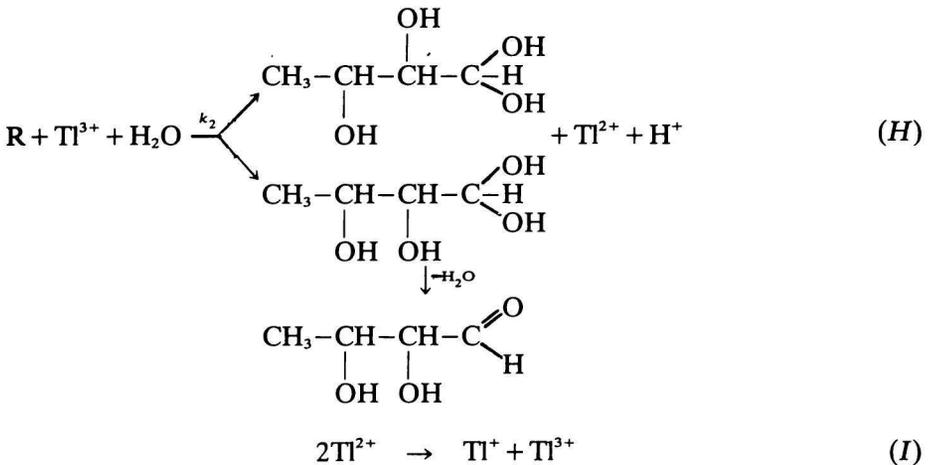
The above reaction scheme leads to the kinetics of the second-order reaction with respect to the Tl(III) ions if $k_1 = 2k_2$, as it is, for instance, in saponification of the glycerol ester diacetate [18]. The radical mechanism is also indicated by the experiments with acrylonitrate as well as by the relatively low value of activation enthalpy. The partial first order observed at the concentration ratio of substrate to the Tl(III) ions $c_s : c_{Tl(III)} = 1.6$—5 for crotonaldehyde and at the concentration ratio 1.6 for methacrolein corresponds to an interstage between the two above-mentioned cases.

The observation that the reaction rate does not practically depend on ionic strength is in agreement with the above mechanism. The observed influence of the hydrogen ions is obviously related to the acid-catalyzed hydration and enolization of crotonaldehyde and methacrolein.

The experiments concerning the influence of the binary water–dioxan mixture show that the plot of the logarithm of rate constant against $1/\varepsilon$ is linear in the interval of the values of dielectric constant 61.8—78.8 for crotonaldehyde and 56—78.8 for methacrolein. The deviation from linearity at higher concentrations of dioxan may be due to a change in solvation of the Tl(III) ions as well as a change in hydration rate of substrate. By using the *Amis* relation [19], we determined the value of critical distance $r = 0.33$ nm for crotonaldehyde and $r = 0.48$ nm for methacrolein from that linear progress. This value is likely to correspond to the distance between the Tl(III) ions and the double bond in the intermediary π complex.

References

1. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Pergamon Press, Oxford, 1966.
2. Lee, A. G., *The Chemistry of Thallium*. Elsevier, London, 1971.
3. Bhatnagar, R., Bhatnagar, M. L., and Mathur, N. K., *J. Electroanal. Chem. 4*, 128 (1962).
4. McKillop, A. and Taylor, E. C., *Endeavour 36*, 88 (1976).
5. McKillop, A., *Pure Appl. Chem. 43*, 463 (1975).
6. Strašak, M., *Chem. Listy 72*, 673 (1978).
7. Henry, P. M., *Advan. Chem. Ser. 70*, 126 (1968).
8. Henry, P. M., *J. Amer. Chem. Soc. 87*, 990, 4423 (1965).
9. Henry, P. M., *J. Amer. Chem. Soc. 88*, 1597 (1966).
10. Uemura, S., Kito, R., and Ichikava, K., *Nippon Kagaku Zasshi 87*, 986 (1966); *Chem. Abstr. 65*, 19962 (1966).
11. McKillop, A., Hunt, J. D., Kienzle, F., Bigham, E., and Taylor, E. C., *J. Amer. Chem. Soc. 95*, 3635 (1973).
12. Watanabe, I., Tanaka, K., and Aoshima, A., *Japan Kokai* 75112315; *Chem. Abstr. 84*, 16779*t* (1976).
13. Watanabe, I., Tanaka, K., and Aoshima, A., *Japan Kokai* 75112314; *Chem. Abstr. 84*, 43315*h* (1976).
14. Treindl, Ľ. and Melicherčík, M., *Collect. Czech. Chem. Commun. 45*, 1173 (1980).
15. Korenman, I. M., *Analiticheskaya khimiya tallia*. Izd. Akad. Nauk SSSR, Moscow, 1960.
16. Perrin, D. D., Armagero, W. L. F., and Perrin, D. R., *Purification of Laboratory Chemicals*. Pergamon Press, Oxford, 1966.
17. Land, H. and Waters, W. A., *J. Chem. Soc. 1957*, 4312.
18. Meyer, J., *Z. Phys. Chem. 67*, 272 (1909).
19. Amis, E. S., *Solvent Effects on Reaction Rates and Mechanisms*. Academic Press, New York, 1966.

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