

KINETICS AND MECHANISM OF THE REDOX REACTION OF THALLIC SULPHATE WITH ACROLEINE

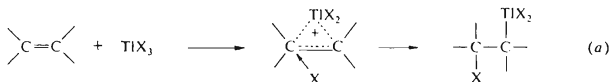
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The stoichiometry, kinetics and mechanism of the redox reaction of thallic sulphate with acroleine in aqueous sulphuric acid or in aqueous dioxane solutions were studied. The acroleine molecule is oxidised with Tl(III) ions in two consecutive one-electron steps to glyceraldehyde. The corresponding rate equation is $-d[\text{Tl(III)}]/dt = k[\text{Tl(III)}]^n [\text{A}]$, where $n = 0-2$. The zeroth reaction order with respect to thallic ions is attributed to a slow enolization of the hydrated acroleine, which is the rate-determining step preceding the redox reaction proper.

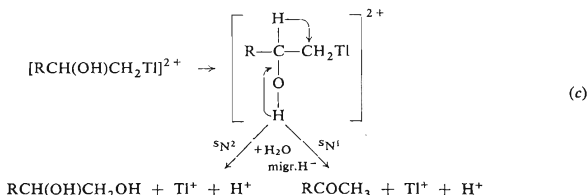
Redox reactions of Tl(III) ions were described in several reviews¹⁻⁵. The work of Henry is especially worth mentioning⁶. Numerous studies were devoted to oxidation of alkenes, which serve as starting materials for the production of carbonyl compounds, mainly solvents. Oxidation of alkenes with Tl(III) ions was studied both from the preparative⁷⁻⁹ and theoretical points of view¹⁰⁻¹⁴. The assumed reaction mechanism is as follows:



Hydroxythallation proceeds in aqueous solution according to



Decomposition of the oxythallic adduct proceeds under formation of glycol and carbonyl. We have to deal with two concurrent reactions, namely solvolytic splitting of the C-Tl bond leading to the formation of glycol or diether, and $\text{C}^2 \rightarrow \text{C}^1$ hydride rearrangement under formation of an oxonium ion yielding a carbonyl compound^{6,12,15}:



Some α,β -unsaturated carbonyl compounds, $\text{ArCH}=\text{CHBr}$ and $\text{CH}_2=\text{CHCN}$, do not undergo oxidation with Tl(III) ions^{4,16}. Sometimes it is possible to carry out oxidation at an elevated temperature and longer reaction time, which however leads to the formation of a mixture of ill-defined products⁹.

Watanabe and coworkers¹⁷ studied the oxidation of unsaturated aliphatic aldehydes of the type $\text{R}^1\text{CH}=\text{CR}^2\text{CHO}$ (R^1, R^2 denote H or CH_3) with Tl(III) ions in aqueous acetic acid or alcohols (R^3OH , where R^3 denotes a C_1 to C_3 alkyl) and found that the oxidation does not take place on olefinic carbon atoms but the CO group is oxidised to COOH under formation of $\text{R}^1\text{CH}=\text{CR}^2\text{COOH}$ or $\text{R}^1\text{CH}=\text{CR}^2\text{COOR}^3$. Since the formed acids or esters are monomers of various polymers, we decided to study the given reactions in more detail in order to elucidate their mechanism. The kinetics of oxidation of acroleine with Tl(III) ions is studied as a special case of redox reactions influenced by binary mixtures.

EXPERIMENTAL

Kinetics. The kinetics of oxidation of acroleine with thallium(III) sulphate in aqueous sulphuric acid was studied polarographically by recording the time dependence of the limiting diffusion current of Tl(III) ions at 0 V vs $1\text{M-Hg}_2\text{SO}_4$ electrode. The indicator electrode was vibrating platinum wire at a frequency of 50 Hz (12 mm in length and 0.5 mm in diameter). A Radelkis OH 102 polarograph and a tempered Kalousek cell were used. The cell temperature was maintained constant to within $\pm 0.05^\circ\text{C}$ by means of a U 10 type thermostat (Medingen, Dresden).

Chemicals. A solution of $\text{Tl}_2(\text{SO}_4)_3$ was prepared by electrochemical oxidation of 200 ml of $0.1 \cdot 10^{-2}\text{M-Tl}_2\text{SO}_4$ of reagent grade (Lachema, Brno) in $0.1\text{M-H}_2\text{SO}_4$ of reagent grade (Lachema, Brno) in an electrolyser of 250 ml holding capacity at room temperature with Winkler type electrodes. The anodic and cathodic compartments were separated by an S4 glass frit. The applied voltage was 2 V, the solution was electromagnetically stirred and the duration of electrolysis was 5 h. In this way we prepared a solution of $1.5 \cdot 10^{-3}\text{M-Tl}_2(\text{SO}_4)_3$ in $0.1\text{M-H}_2\text{SO}_4$. The concentration of Tl(III) ions was determined iodometrically¹⁸. Acroleine (pure, Fluka) was distilled on a Vigreux type column in nitrogen atmosphere¹⁹; the fraction boiling at $51.5-52.5^\circ\text{C}$ was taken. It was stored in nitrogen atmosphere in a refrigerator. The preparation of acroleine solutions, their handling and the measurements were done in a nitrogen atmosphere. The measurements were done not later than 24 h after distillation. Solutions were made from redistilled water, other chemicals and solvents were of reagent grade (Labora, Brno). The reaction stoichiometry was determined by polarometric titration.

Analysis of reaction products. When the reaction was finished, Tl^+ ions were precipitated with HCl and thallium chloride was filtered off. A saturated solution of 2,4-dinitrophenylhydrazine in 2M-HCl was added to the aqueous solution. After standing for 3 days at room temperature, the yellow-brown precipitate was filtered off and dissolved in benzene, the solution was evaporated to 50 ml volume and chromatographed on a silicagel column (L 100/160, Lachema, Brno) which was 40 cm long and 3 cm wide. After elution with benzene, three large zones appeared, the first of which moved rapidly; by concentrating this fraction we obtained the substance *I* melting at $166-7^\circ\text{C}$ and forming orange crystals. The second zone moved more slowly and by concentrating this fraction we obtained a yellow crystalline substance *II* melting at $312-313^\circ\text{C}$. The third

zone separated at the end of the column into several small zones, from which we could not isolate any crystalline substance owing to the small amount available. Elementary analysis revealed the following composition for substance *I*: 45.62% C, 3.29% H, 24.00% N. The calculated composition for $C_9H_8O_4N_4$ is 45.76% C, 3.41% H, 23.72% N. For substance *II* we found 41.03% C, 2.91% H, 25.44% N, while the calculated composition for the assumed formula $C_{15}H_{12}O_8N_8$ is 41.57% C, 2.79% H, 25.85% N. Thin-layer chromatography on silufol (UV 254, Glass Works Kavalier) with benzene as eluent showed distinct spots.

The absence of acrylic acid in the reaction mixture was proved by capillary isotachoforesis²⁰. Barium hydroxide was added to the reaction mixture and the precipitate of $BaSO_4$ was removed by centrifugation. The supernatant was injected (10 μ l) into the separating compartment. The detection limit is under these conditions smaller than 10^{-4} M, hence acrylic acid could not be formed in a larger quantity than 10% with respect to the concentration of the reaction products. 0.01 M-HCl titrated with ϵ -aminocaproic acid to pH 4.5 was used as leading electrolyte, 0.2% hydroxyethylcellulose was used as additive, and about 10^{-3} M capronic acid as terminating electrolyte. Acrylic acid as standard was treated analogously²¹.

RESULTS

The redox reaction of Tl(III) ions with acroleine is of zero order with respect to Tl(III) ions in the range of $5.5 \cdot 10^{-3}$ – $6.5 \cdot 10^{-2}$ M acroleine in 0.1 M- H_2SO_4 at 17.5°C in the presence of $7.5 \cdot 10^{-4}$ M $Tl_2(SO_4)_3$. The reaction order was determined by the integral method. Under these conditions the experimental rate constant was determined as $k = 2.3 \cdot 10^{-4} s^{-1}$. At lower acroleine concentrations, the reaction order with respect to Tl(III) increases as shown in Table I.

In the presence of $5.5 \cdot 10^{-3}$ – $6.5 \cdot 10^{-2}$ M acroleine, the rate equation can be written as

$$-d[Tl(III)]/dt = k[Tl(III)]^0 [A] = k[A]. \quad (1)$$

The limiting diffusion current is

$$I = \kappa[Tl(III)], \quad (2)$$

hence

$$-dI/dt = \kappa k[A] = k'[A], \quad I = -k'[A]t + I_0, \quad (3), (4)$$

The measured dependence of the limiting diffusion current on time is indeed linear and from its slope the rate constant k was determined.

At lower acroleine concentrations than $5.5 \cdot 10^{-3}$ M, the rate equation has the form

$$-d[Tl(III)]/dt = k'[Tl(III)]^n [A], \quad (5)$$

where $n = 1-2$ depending on the acroleine concentration (Table I).

In the region where the reaction is of zeroth order with respect to $Tl(III)$, we studied the dependence of the rate constant on pH at constant ionic strength ($I = 0.15M$) and practically constant concentration of HSO_4^- ions. We found the relation

$$k = k_0 + k_{H_3O^+} [H_3O^+]. \quad (6)$$

The values of $k_0 = 0.56 \cdot 10^{-4} s^{-1}$ and $k_{H_3O^+} = 1.74 \cdot 10^{-3} dm^3/mol s$ were determined by the least squares method.

TABLE I

Dependence of Reaction Order (n) with Respect to $Tl(III)$ on Acrolein Concentration
 $7.5 \cdot 10^{-4}M-Tl_2(SO_4)_3$; $0.1M-H_2SO_4$; $17.5^\circ C$.

c, M	n	Rate constant
$6.5 \cdot 10^{-2}$	0	$k = 2.3 \cdot 10^{-4} s^{-1}$
$5.5 \cdot 10^{-2}$	0	
$4.5 \cdot 10^{-2}$	0	
$3.5 \cdot 10^{-2}$	0	
$2.5 \cdot 10^{-2}$	0	
$1.5 \cdot 10^{-2}$	0	
$7.5 \cdot 10^{-3}$	0	
$5.5 \cdot 10^{-3}$	0	$k_{exp} = 3.2 \cdot 10^{-4} s^{-1}$
$2.5 \cdot 10^{-3}$	1	
$1.5 \cdot 10^{-3}$	2	$k' = 0.12 dm^3 mol^{-1} s^{-1}$
		$k' = 0.17 dm^3 mol^{-1} s^{-1}$

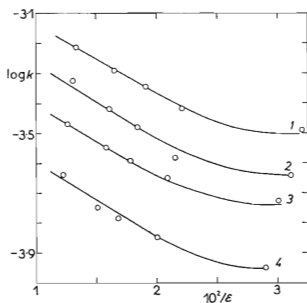


FIG. 1
 Dependence of Logarithm of Rate Constant
 on Reciprocal Dielectric Constant in Water-
 Dioxane Mixtures
 Temperatures: 1 35; 2 30; 3 25; 4 $17.5^\circ C$.

TABLE II

Dependence of Rate Constant on Temperature in Water-Dioxane Mixtures
 $7.5 \cdot 10^{-4} \text{M-Tl}_2(\text{SO}_4)_3$; $0.1 \text{M-H}_2\text{SO}_4$; x = mole fraction of dioxane.

$t, ^\circ\text{C}$	x	$k \cdot 10^4, \text{s}^{-1}$
17.5	0	2.3
25	0	3.4
30	0	4.8
35	0	6.1
17.5	0.039	1.8
25	0.039	2.8
30	0.039	3.8
35	0.039	5.1
17.5	0.063	1.6
25	0.063	2.5
30	0.063	3.3
35	0.063	4.5
17.5	0.094	1.4
25	0.094	2.2
30	0.094	2.6
35	0.094	3.8
17.5	0.174	1.1
25	0.174	1.9
30	0.174	2.3
35	0.174	3.3

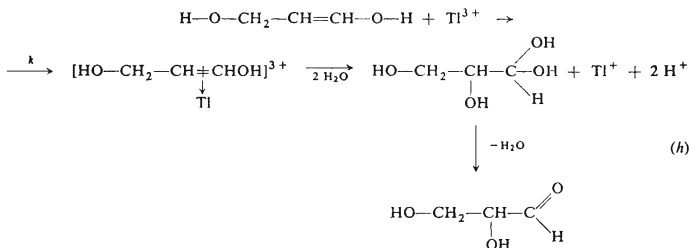
TABLE III

Activation Parameters in Water-Dioxane Mixtures

$7.5 \cdot 10^{-4} \text{M-Tl}_2(\text{SO}_3)_2$; $0.1 \text{M-H}_2\text{SO}_4$; x = mole fraction of dioxane.

x	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J K}^{-1} \text{mol}^{-1}$
0	35.9	-191
0.039	37.5	-187
0.063	37.2	-189
0.094	36.8	-192
0.174	37.8	-190

In the presence of Tl(III) ions in solution, oxidation of the hydrated enol form proceeds:



The rate equation

$$-d[\text{Tl(III)}]/dt = k[\text{Tl(III)}][\text{E}] \quad (7)$$

corresponds to the redox reaction (h). The observed zeroth reaction order can be elucidated on the assumption that the rapid redox step (h) is preceded by the slow enolization (g), which is probably the rate-determining step. We assume the stationary state,

$$d[\text{E}]/dt = 0, \quad (8)$$

in the prevailing portion of the reaction course. Then, with respect to the assumed reaction mechanism, we have

$$k_-[\text{K}] - k[\text{E}]\text{Tl(III)} = 0, \quad (9)$$

whence

$$[\text{E}]_s = k_-[\text{K}]/k[\text{Tl(III)}]. \quad (10)$$

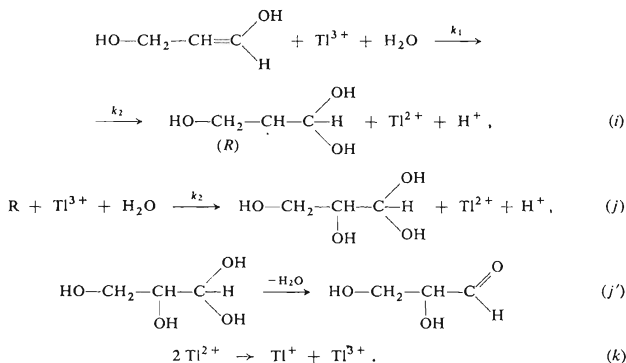
If we substitute this value for the concentration of the enol form in Eq. (7), we obtain

$$-d[\text{Tl(III)}]/dt = k_-[\text{K}], \quad (11)$$

whence it is seen that the reaction is of zeroth order with respect to Tl(III) ions and that the term $k_-[\text{K}]$ is constant at a sufficient excess of the substrate.

At a ratio of acroleine to Tl(III) ions 1 : 1, the reaction order with respect to Tl(III) ions is 2. In this case the acroleine concentration is no more sufficient to attain the

stationary state and its oxidation proceeds apparently in two consecutive steps:



This reaction scheme leads to a second-order kinetics with respect to Ti^{3+} ions if $k_1 = 2k_2$ as, e.g., in the hydrolysis of glycerine diacetate²³. Experiments with acrylonitrile and a relatively low value of the activation enthalpy are also in support of the radical mechanism.

At a concentration ratio of acroleine to Ti^{3+} ions 1.6 : 1, the measured reaction order of 1 is intermediate between the two mentioned cases.

The mentioned reaction mechanism is in accord with the fact that the reaction rate is practically independent of the ionic strength. The observed influence of pH apparently corresponds to an acid-catalysed hydration and enolization of acroleine.

Experiments with water-dioxane binary mixtures show that the dependence of the logarithm of the rate constant on $1/\epsilon$ is linear in the interval of ϵ values from 78.8 to 55.5. At higher dioxane concentrations, the deviation from the linear dependence can be attributed to a change in the solvation of Ti^{3+} ions and also to a different hydration rate of acroleine. We determined from the mentioned linear course using the Amis' equation²⁴ the critical distance $r = 0.43$ nm which probably corresponds to the distance between the Ti^{3+} ion and the double bond in the intermediate π -complex.

Analysis of the reaction mixture suggests in accord with the assumed reaction mechanism that the oxidation of acroleine with Ti^{3+} ions proceeds *via* the mentioned π -complex and not through oxidation of the CO group.

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