

Kinetics and salt effects in the oxidation of pentanones by thallium(III) salts in aqueous medium

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The kinetics of oxidation of pentanones by thallium(III) salts in aqueous medium was investigated by ultraviolet spectrophotometry at concentrations of 10^{-4} — 10^{-2} mol dm⁻³ and iodometrically at concentrations of about 3×10^{-1} mol dm⁻³. In the first case, the influence of concentration of inert electrolyte and ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ on the rate of reaction was also studied. It was found that the rate of oxidation of 3-pentanone did not depend on ionic strength and increased exponentially with decreasing ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ at constant ionic strength. In the second case, influence of concentration of Li₂SO₄ and NaClO₄ on the selectivity of reaction was studied at higher concentrations of reactants. The ratio of mole fractions of both main reaction products of oxidation of 2-pentanone, i.e. 3-hydroxy-2-pentanone and 1-hydroxy-2-pentanone, increased with concentration of Li₂SO₄ and decreased with increasing concentration of NaClO₄.

Кинетика окисления пентанонов таллиевыми солями в водной среде изучалась УФ-спектрофотометрически при концентрациях 10^{-4} — 10^{-2} моль дм⁻³ и иодометрически при концентрациях близких $3 \cdot 10^{-1}$ моль дм⁻³.

В первом случае изучалось также влияние концентрации инертного электролита и отношения $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ на скорость реакции. Было найдено, что скорость окисления 3-пентанона не зависит от ионной силы

и что при снижении отношения $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ при постоянной ионной силе скорость реакции экспоненциально возрастает. Во втором случае при более высоких концентрациях реагентов изучалось влияние концентрации Li_2SO_4 и NaClO_4 на скорость и селективность реакции. Скорость реакции сильно падает при повышении концентрации Li_2SO_4 и слегка возрастает при повышении концентрации NaClO_4 . Отношение мольных долей обоих главных продуктов окисления 2-пентанона, то есть 3-гидрокси-2-пентанона и 1-гидрокси-2-пентанона, повышается при увеличении концентрации Li_2SO_4 и понижается при повышении концентрации NaClO_4 .

Thallium(III) ions are specific agents in a great number of organic syntheses [1, 2]. The oxidation of unsaturated compounds with multiple bonds fast localized [3, 4] or compounds existing in two tautomeric oxo-enol forms [5] belongs among these reactions. The oxidation of cyclic ketones in aqueous medium [6] gives rise to α -hydroxycycloalkanones or cycloalkane carboxylic acid the ring of which is reduced by one carbon atom compared to the starting ketone. Aliphatic ketones are oxidized by thallium(III) acetate in acetic acid to give α -acetoxyketones [7] while the oxidation by thallium(III) nitrate in acetonitrile gives rise to α -nitrates of ketones [8]. On the other hand, the oxidation of aliphatic ketones by thallium(III) sulfate in aqueous medium affords α -hydroxyketones [9]. The course of oxidation of ketones may be described by kinetic equation of the first order [7, 10] or by the second order [10—12].

The salt effects were investigated only in the oxidation of some aliphatic ketones, cyclopentanone [11], and acetophenone [12] by thallium(III) acetate in dilute acetic acid. In the first case, the reaction rate initially increases proportionally with concentrations of inert electrolytes (HSO_4^- and ClO_4^- ions). However, this increase is proportional to the squared power of electrolyte concentration provided the concentration of inert electrolytes exceeds 1.5 mol dm^{-3} . In the second case, no influence of Na_2SO_4 or NaClO_4 addition on the rate of oxidation was observed. Since the influence of inert electrolyte concentration was ascertained only in a few cases and the data as well as the results of kinetic measurements were inconsistent, we considered necessary to study the kinetics of oxidation of aliphatic ketones by thallium(III) sulfate in the presence of sulfuric acid and to investigate the influence of concentration of the sulfate and perchlorate anions on the rate and selectivity of reaction at two different concentrations of the oxidation agent.

Experimental

Chemicals

The solution of thallium(III) sulfate and both ketones were prepared by the methods described earlier [13, 14]. The solution of thallium(III) perchlorate was prepared by

dissolving freshly precipitated thallium(III) hydroxide in dilute perchloric acid at boiling. Thallium(III) hydroxide was precipitated from the solution of thallium(III) sulfate in dilute sulfuric acid and sulfate anions were removed by repeated washing with distilled water. Other chemicals were pure or anal. grade commercial products (Lachema, Brno).

Analysis of the oxidation products

For determining the selectivity of formation of the oxidation products, the experiments were carried out at a relatively high initial concentration of thallium(III) sulfate, the standard conditions being: a) 150 cm³ of Tl₂(SO₄)₃ solution ($c = 0.13 \text{ mol dm}^{-3}$), corresponding quantity of ketone, $c(\text{H}_2\text{SO}_4) = 1.51 \text{ mol dm}^{-3}$, $c(\text{Li}_2\text{SO}_4) = 0\text{--}2 \text{ mol dm}^{-3}$, and temperature of 50°C; b) 150 cm³ of Tl₂(SO₄)₃ solution ($c = 0.145 \text{ mol dm}^{-3}$), corresponding quantity of ketone, $c(\text{H}_2\text{SO}_4) = 1.08 \text{ mol dm}^{-3}$, $c(\text{NaClO}_4) = 0\text{--}2.87 \text{ mol dm}^{-3}$, and temperature of 35°C. The determination of thallium(I) and thallium(III) ions, isolation and identification of the reaction products were described in more detail previously [9].

Kinetic methods

The kinetic measurements were carried out in an isothermal discontinuous reactor in glass ampoules. The initial concentrations of substrates were: $[\text{Tl}^{3+}]_0 = 2.91 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{ketone}]_0 = 1.46 \times 10^{-3}\text{--}1.16 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_3\text{O}^+] = 2 \times 10^{-1} \text{ mol dm}^{-3}$. The influence of ionic strength on the rate of reaction was studied in three series of experiments under these conditions. In the first two series of experiments, the ionic strength of solution was adjusted in the range ΔI 0—3 mol dm⁻³ by adding the inert electrolyte, i.e. Li₂SO₄ or NaClO₄. In the third series, the dependence of the rate constant on the ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ was investigated at constant ionic strength of 3.3 mol dm⁻³. The reaction temperature used was held constant within accuracy $\pm 0.1^\circ\text{C}$. The kinetics of oxidation was investigated by ultraviolet spectrophotometry (Specord UV VIS, Zeiss, Jena) in the region of 210—280 nm by measuring the decrease in absorbance which corresponds to the decrease in concentration of Tl³⁺. The thallium(III) ions were determined on adding a considerable excess of the chloride anions in the form of $[\text{TlCl}_6]^{3-}$ [15].

Results

Analysis of oxidation products

The course of reaction at relatively high concentrations of Tl(III) and ketone (about 0.3 mol dm⁻³) is represented for both pentanones in Fig. 1. The oxidation was carried out at constant ionic strength of solution (7.77 mol dm⁻³).

The influence of concentration of inert electrolyte on the rate of oxidation was described in more detail previously [9].

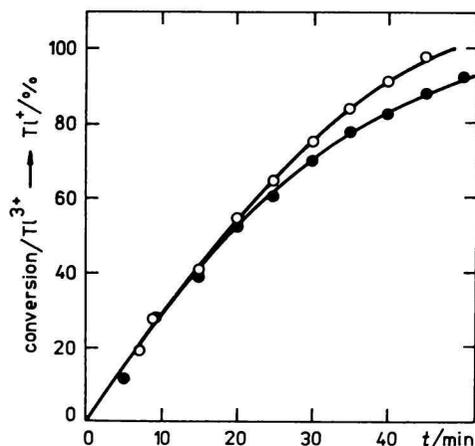


Fig. 1. Variation of $Tl^{3+} \rightarrow Tl^+$ conversion with time for the oxidation of pentanones by thallium(III) sulfate.

$c(H_2SO_4) = 1.51 \text{ mol dm}^{-3}$, $\Theta = 50^\circ\text{C}$.

○ 2-Pentanone; ● 3-pentanone.

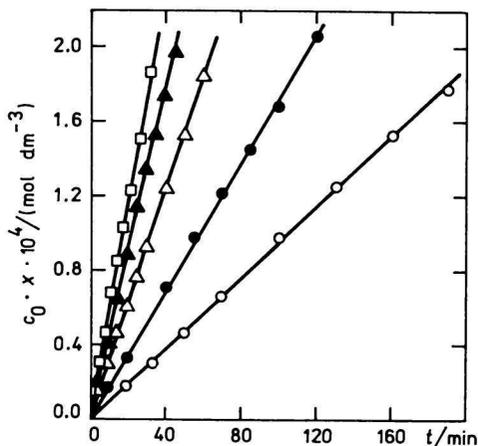


Fig. 2. Concentration of Tl^+ as a function of time for the oxidation of 2-pentanone by a solution of thallium(III) sulfate ($\Theta = 50^\circ\text{C}$).

$[Ketone]_0$: ○ $1.46 \times 10^{-3} \text{ mol dm}^{-3}$; ● $2.91 \times 10^{-3} \text{ mol dm}^{-3}$; △ $5.83 \times 10^{-3} \text{ mol dm}^{-3}$; ▲ $8.74 \times 10^{-3} \text{ mol dm}^{-3}$; □ $1.16 \times 10^{-2} \text{ mol dm}^{-3}$.

3-Hydroxy-2-pentanone and 1-hydroxy-2-pentanone were identified as main products of the oxidation of 2-pentanone [16]. The influence of ionic strength on the selectivity of reaction is demonstrated in Table 1.

Table 1

Influence of ionic strength on the distribution of α -hydroxypentanones (x_3/x_1)

Electrolyte	$[H_2SO_4]/(\text{mol dm}^{-3})$	$\Theta/^\circ\text{C}$	$\Delta I/(\text{mol dm}^{-3})$				
			0	1.43	2.87	3.30	5.00
Li_2SO_4	1.51	50	4.77	—	—	6.13	7.21
$NaClO_4$	1.08	35	6.12	3.81	2.80	—	—

x_3 and x_1 represent the mole ratios of 3-hydroxy-2-pentanone and 1-hydroxy-2-pentanone.

Kinetic measurements

The course of oxidation of both pentanones by thallium(III) sulfate at concentrations suited to spectral technique is represented in Figs. 2 and 3. The values of rate constants calculated from these kinetic data are given in Table 2.

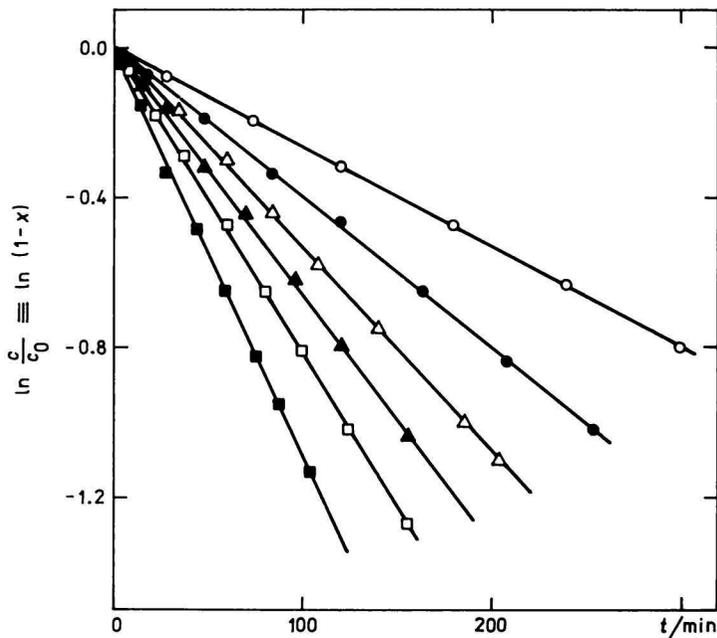


Fig. 3. Value of $\ln ([\text{Ti}^{3+}]/[\text{Ti}^{3+}]_0)$ as a function of time for the oxidation of 3-pentanone by a solution of thallium(III) sulfate ($\Theta = 40^\circ\text{C}$).

$[\text{Ketone}]_0$: ○ $2.91 \times 10^{-3} \text{ mol dm}^{-3}$; ● $4.37 \times 10^{-3} \text{ mol dm}^{-3}$; △ $5.83 \times 10^{-3} \text{ mol dm}^{-3}$; ▲ $7.28 \times 10^{-3} \text{ mol dm}^{-3}$; □ $8.74 \times 10^{-3} \text{ mol dm}^{-3}$; ■ $1.16 \times 10^{-2} \text{ mol dm}^{-3}$.

Table 2

Values of the observed and real rate constants for oxidation of pentanones by a solution of thallium(III) sulfate

$[\text{Ketone}]_0$ mol dm^{-3}	2-Pentanone (50 °C)		3-Pentanone (40 °C)	
	$\frac{k_{\text{obs}}^0 \cdot 10^8}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$\frac{k_1 \cdot 10^6}{\text{s}^{-1}}$	$\frac{k_{\text{obs}}^1 \cdot 10^4}{\text{s}^{-1}}$	$\frac{k_{11} \cdot 10^2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
1.46×10^{-3}	1.427	9.774	—	—
2.91×10^{-3}	2.854	9.807	0.453	1.557
4.37×10^{-3}	—	—	0.699	1.600
5.83×10^{-3}	5.085	8.722	0.902	1.547
7.28×10^{-3}	—	—	1.073	1.474
8.74×10^{-3}	7.317	8.372	1.377	1.576
1.16×10^{-2}	9.873	8.511	1.846	1.591

The presence of salt effects was studied in the oxidation of 3-pentanone. It was revealed that the rate of reaction did not depend on the concentration of neutral electrolyte, but it changed with the ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$, as evident from Fig. 4.

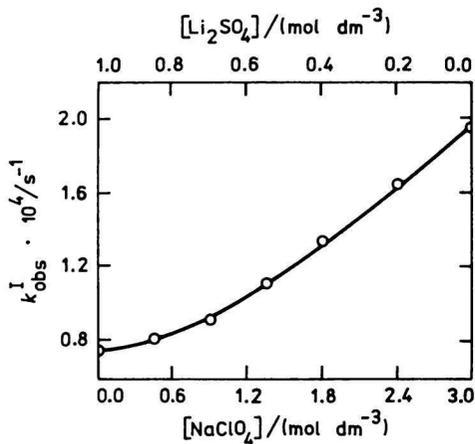


Fig. 4. Influence of the ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ on the observed rate constant of oxidation of 3-pentanone by thallium(III) sulfate. $[\text{Ketone}]_0 = 2.31 \times 10^{-3} \text{ mol dm}^{-3}$, $\Theta = 45^\circ\text{C}$.

Table 3

Activation parameters for oxidation of pentanones by thallium(III) sulfate

Ketone	E^a kJ mol ⁻¹	A^a mol dm ⁻³ s ⁻¹	ΔH^{*b} kJ mol ⁻¹	ΔS^{*b} J mol ⁻¹ K ⁻¹
2-Pentanone	74.4	2.30×10^8	96.8	-42.0
3-Pentanone	82.3	4.07×10^9	100.9	+42.1

a) Concentration of ketone 0.35 mol dm^{-3} .

b) Concentration of ketone $2.91 \times 10^{-3} \text{ mol dm}^{-3}$.

The values of activation parameters of the oxidation of 2-pentanone and 3-pentanone in both investigated concentration regions are given in Table 3.

Discussion

Recently [9], we stated that the investigated oxidation of isomeric pentanones proceeded at the concentrations of reactants of about 0.3 mol dm^{-3} in the transition zone between the diffusion and kinetic region while the oxidation of higher (C-6—C-8) ketones took place in the diffusion region. The concentration of ketones used is near to the limit of solubility of pentanones in the oxidation solution. That is also upheld by the shape of kinetic curves in Fig. 1 as well as by the

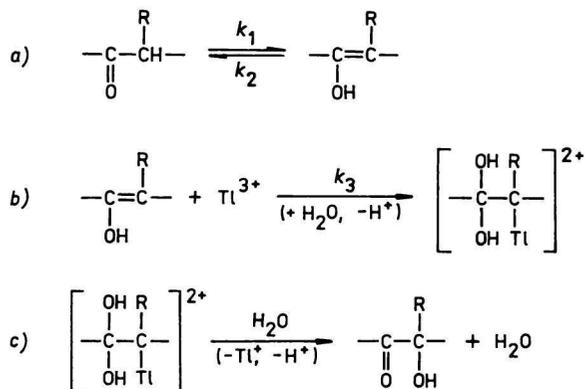
comparison of apparent and real energies of activation of oxidation (Table 3). In the above-mentioned study we observed a relatively conspicuous influence of concentration of neutral electrolytes on the rate of reaction. In this case, the kinetics of oxidation must be also determined by other factors than the kinetic ones.

It is obvious from the results presented in Figs. 2 and 3 and Table 2 that the kinetic behaviour of both pentanones in oxidation in homogeneous phase is different, which is also confirmed by the investigated dependence of the reaction rate on the concentration of Tl(III) [10]. As a sufficient excess of ketone with respect to Tl^{3+} was used, the kinetic order was decreased by 1. The oxidation of 2-pentanone may be described by a kinetic equation of the pseudo-zero order (eqn (1)) while the oxidation of 3-pentanone obeys a kinetic equation of the pseudo-first order (eqn (2)).

$$\frac{-d [Tl^{3+}]}{dt} = k_I [2\text{-pentanone}] = k_{obs}^0 \quad (1)$$

$$\frac{-d [Tl^{3+}]}{dt} = k_{II} [3\text{-pentanone}] [Tl^{3+}] = k_{obs}^I [Tl^{3+}] \quad (2)$$

The investigated oxidation involves three successive steps [6, 10]: a) oxo-enol tautomeric equilibrium, b) oxythallation, and c) decomposition of the oxythallic adduct (Scheme 1).



Scheme 1

The different kinetic behaviour of both ketones in oxidation may be explained by different stability of their enols (structures I and II).



As for the oxidation of 2-pentanone, the rate of oxythallation is substantially higher than the rate of conversion of enol into keto form, which means $k_2 \ll k_3$ [Ti^{3+}]. Then assuming a stationary state, it holds $k_1 = k_1$ [10]. As for the oxidation of 3-pentanone, the situation is reverse: $k_2 \gg k_3$ [Ti^{3+}] and hence $k_{11} = k_1 k_3 / k_2$. In conformity with published data [7] the oxo-enol tautomeric equilibrium is the rate-determining step of oxidation not only for methylalkyl ketones ($\text{R}^2 > \text{CH}_3$) but also for dialkyl ketones ($\text{R}^1, \text{R}^2 > \text{CH}_3$) [10]. In order to verify this fact we investigated the kinetics of oxidation of dialkyl ketone in the presence of varying amount of neutral electrolyte. The influence of concentration of Li_2SO_4 and NaClO_4 on the reaction rate was determined for the oxidation of 3-pentanone. The near values of the rate constants observed for ionic strength of solution varying in the range 0.3—3.3 mol dm⁻³ (found for Li_2SO_4 : $k_{\text{obs}}^1 \times 10^5 = (7.26 \pm 0.29) \text{ s}^{-1}$; found for NaClO_4 : $k_{\text{obs}}^1 \times 10^4 = (2.13 \pm 0.03) \text{ s}^{-1}$) indirectly confirm that the Ti^{3+} ions do not participate in the rate-determining step of the reaction. It is a significant difference when compared with the oxidation of alkenes by the same agent [17] for which a decrease in the rate of reaction with increasing concentration of Li_2SO_4 was observed. In this case, the oxythallation (more correct π — σ isomerization of the organothallic adduct) is the rate-determining step of reaction. It results from the comparison of the mentioned rate constants that the rate of oxidation in the perchlorate oxidation system is greater than in the sulfate oxidation system ($k_{\text{ClO}_4^-} : k_{\text{SO}_4^{2-}} \doteq 3$). Similarly, the rate of oxidation increases with decreasing ratio $x(\text{SO}_4^{2-})/x(\text{ClO}_4^-)$ at constant ionic strength (Fig. 4).

The influence of Li_2SO_4 and NaClO_4 concentration on the ratio 3-hydroxy-2-pentanone/1-hydroxy-2-pentanone in the oxidation products of 2-pentanone (Table 1) is different. The increase in concentration of Li_2SO_4 promotes the yield of 3-hydroxy-2-pentanone whereas the addition of NaClO_4 has opposite effect. More significant changes in selectivity of the reaction due to addition of electrolyte were observed in the use of NaClO_4 .

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