Oxidation of isomeric 2,4,4-trimethylpentenes by thallium(III) sulfate in aqueous medium

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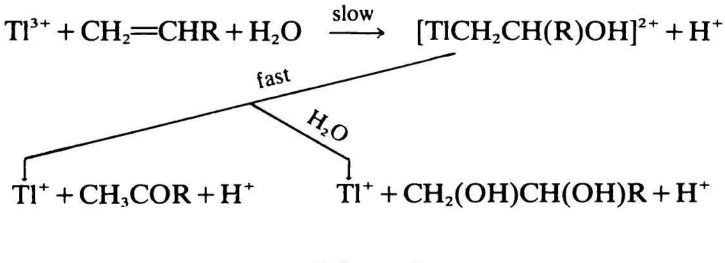
The course, conditions, and characteristics of the products of oxidation of 2,4,4-trimethyl-1- and -2-pentene by thallium(III) sulfate in aqueous solution of sulfuric acid were studied. Among the parameters particularly the influence of temperature, the structure of the starting olefins, and the molar ratio olefin/Tl^{3+} on the reaction rate and the selectivity was studied.

The main products of the oxidation were carbonyl compounds and corresponding vicinal glycols. Under certain conditions also consecutive products of a condensation character were produced.

Были изучены протекание, условия и характер продуктов окисления 2,4,4-триметил-1-пентена и 2,4,4-триметил-2-пентена сульфатом таллия(III) в водном растворе серной кислоты. Среди параметров были исследованы прежде всего влияние температуры, строение исходных олефинов и молярного отношения олефин: Tl^{3+} на скорость реакции и селективность.

Анализом продуктов окисления были обнаружены в качестве главных продуктов карбонильные соединения и соответствующие вицинальные гликолы. В определенных условиях образовались также вторичные продукты конденсационного характера.

The first papers dealing with oxidation of olefins by thallium(III) salts were published in the beginning of the sixties [1—3]. From *Henry*'s basic studies on the course of this reaction in aqueous medium [4, 5] it is evident that this reaction can be described by Scheme 1



Scheme 1

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It is a second-order reaction and its rate depends on the concentration of the Tl^{3+} ions and olefin [1, 4, 5]

$$-\frac{d[\text{olefin}]}{dt} = -\frac{d[Tl^{3+}]}{dt} = k\,[Tl^{3+}][\text{olefin}].$$

Besides of unbranched olefins oxidized by Tl^{3+} in aqueous [4—6] and methanolic [7, 8] solutions of mineral acids, where carbonyl compounds and vicinal glycols are produced, oxidations of cyclic olefins in aqueous and methanolic solutions [9—12] were studied. The latter undergo an oxidative change under the formation of carbonyl compounds — only aldehydes with a narrowed cycle are formed, with the exception of cyclopentene, from which a non-rearranged product — cyclopentanone — is obtained. Besides also oxidations of chalcones in methanol [13, 14], where isoflavones are obtained, were studied. It seems that the distribution of the products depends to a certain degree on the specific experimental conditions.

This paper is dealing with the oxidation of trimethylpentenes, which can be prepared in high yields by the dimerization of isobutylene.

Experimental

Chemicals

Crude 2,4,4-trimethylpentenes were obtained by distillation of oligomer mixtures of isobutylene (25% of 2,4,4-trimethylpentenes, 10% of portions with lower boiling point, 65% of trimers and others). It consists of two isomers: 2,4,4-trimethyl-1-pentene (*I*) and 2,4,4-trimethyl-2-pentene (*II*) in a ratio about 4 : 1. The individual isomers were separated by an effective rectification; they were obtained in chromatographic purity min. 99.5% (GLC CHROM II, flame ionization detector, capillary column, length 50 m, squalane packing, temperature of the column 80°C, sensibility 1/20, gas flow: H_2 50 ml/min, air 16 ml/min, and overpressure N_2 0.1 MPa).

The solution of thallium(III) sulfate was prepared by electrochemical oxidation of anal. grade (Spolana, Neratovice) in an electrolyzer with a volume of 2 l at room temperature using a lead anode and a carbon cathode. The potential was 4 V. The catholyte was separated from the anolyte by a ceramic cylindrical diaphragm (Karborundum, Benátky n. J.). The electrolyte contained 0.37 M-Tl_2SO_4 and 2 M-H_2SO_4. An electromagnetic stirrer was used. After the oxidation was completed (the presence of Tl^+ ions was checked by means of the reaction with HCl) 0.37 M-$Tl_2(SO_4)_3$ in 1.25 M-H_2SO_4 was obtained.

The standards of vicinal glycols were prepared by oxidation of trimethylpentene by hydrogen peroxide in the presence of OsO_4 catalyst in medium of dry *tert*-butyl alcohol by a modified method [15]. The obtained glycols had following characteristics:

For 2,4,4-trimethyl-1,2-pentanediol (*a*) and 2,4,4-trimethyl-2,3-pentanediol (*b*) $C_8H_{18}O_2$ (146.22)

	% C (calc./found)	% H (calc./found)	M.p., °C	B.p., °C
a	66.71/66.71	12.32/12.35	59.10	216.2
b	66.71/66.62	12.32/12.39	65.30	199.4

Oxidation

To aqueous solution of thallium(III) sulfate (150 ml) in a temperated thermostat the corresponding trimethylpentene (20 ml) was added under stirring. The molar ratio olefin/Tl^{3+} was changed in the range 1/1—5/1, the rotation speed of the stirrer in the range 900—1600 rev./min, and the temperature from 20 to 80°C.

During the reaction, the decrease of Tl^{3+} ions was determined by iodometric titration [16] and from this the conversion was calculated. After the reaction was completed the aqueous and organic layers were separated and weighed. From the aqueous phase Tl^+ was precipitated in the form of insoluble TlCl by an equivalent amount of HCl. The latter product was transformed by boiling with 50% H_2SO_4 into Tl_2SO_4, which was returned to the electrochemical reoxidation.

The qualitative analysis of the reaction mixture was carried out by the spot reactions according to [17]. For the quantitative determination of vicinal glycols in both phases the periodate method [18] was used. The carbonyl compounds were determined by GCMS analysis (GLC FRACTOVAP 2300, C. Erba, Milan, 250 cm column with 2 mm diameter, packing 10% poly(ethylene glycol adipate) on

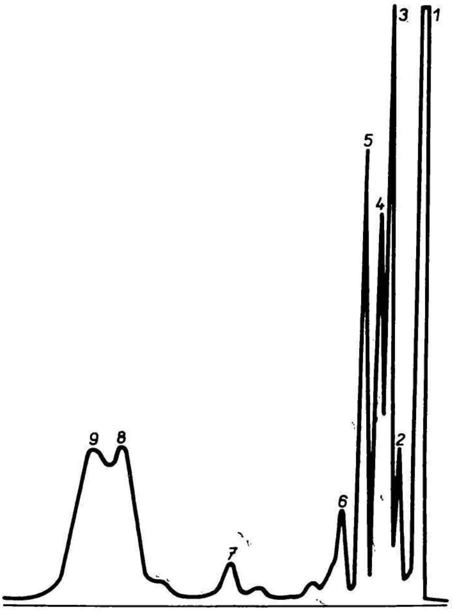


Fig. 1. Chromatogram of the products of oxidation of 2,4,4-trimethyl-1-pentene (molar ratio olefin/Tl^{3+} 2/1, rotation speed of the stirrer 1600 rev./min).

1. 2,4,4-Trimethyl-1-pentene (*I*); *2.* 5,5-dimethyl-3-hexanone (*III*); *3.* 2,4,4-trimethylpentanal (*IV*); *4.* 4,4-dimethyl-2-pentanone (*V*); *5.* 5,5-dimethyl-2-hexanone (*VI*); *6.* C_8 ketone; *7.* C_9 aldol; *8.*, *9.* C_{16} aldolization products.

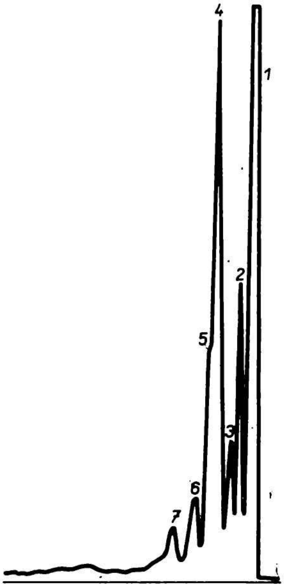


Fig. 2. Chromatogram of the products of oxidation of 2,4,4-trimethyl-2-pentene (molar ratio olefin/Tl^{3+} 2/1, rotation speed of the stirrer 1600 rev./min).

1. 2,4,4-Trimethyl-2-pentene (*II*); *2.* 2,4,4-trimethyl-3-pentanone (*VII*); *3.* 5,5-dimethyl-3-hexanone (*III*); *4.* 3,4,4-trimethyl-2-pentanone (*VIII*); *5.* C_8 ketone; *6.* 5,5-dimethyl-2-hexanone (*VI*); *7.* C_8 ketone.

Chromatone NAW DMCS, temperature of the feeder 175°C, temperature of the column 120°C, sensitivity 1/3.2, feedstock 0.1 μl, gas flow: N_2, 35 ml/min, H_2, 85 ml/min, and air, 75 ml/min; M. S. MAT 111 GNOM Varian, packing column with 3% SE/Varaport, length of the column 1 m, diameter 3 mm, isothermal conditions at 105°C, He flow 13 ml/min, ionization potential 80 eV, intensity 270 mA, temperature of the ionic source 200°C).

Results

Analysis of the oxidation products

Aldehydes, ketones, and vicinal glycols were determined after oxidation of 2,4,4-trimethyl-1-pentene in the organic phase and only vicinal glycols in the aqueous phase. The test for carboxyl acids was negative in both cases. The chromatogram of the organic phase is shown in Fig. 1.

The presence of C_7 ketone proves that also a partial destructive degradation of the thallium complex with the origin olefin takes place, whereby formaldehyde and C_7 ketone are formed. The formed formaldehyde and 2,4,4-trimethylpentanal undergo an aldol condensation, either by a mutual reaction or by a reaction of individual compounds with themselves (peaks *7—9*), obviously in consequence of the strong acid medium (pH < 1) under the formation of aldolization products.

In the organic phase of reaction mixture after the oxidation of 2,4,4-trimethyl-2-pentene only

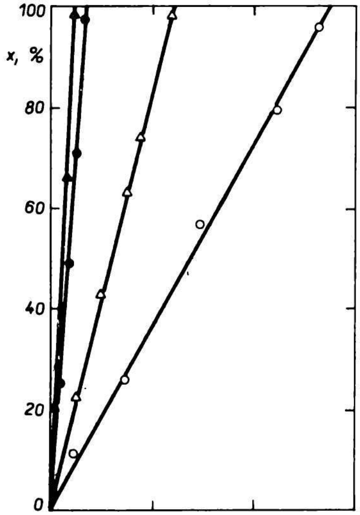


Fig. 3. Dependence of the conversion $Tl^{3+} \rightarrow Tl^+$ on the time in oxidation of 2,4,4-trimethyl-1-pentene (molar ratio olefin/Tl^{3+} 2/1, rotation speed of the stirrer 1600 rev./min).
○ $t = 20°C$; △ $t = 40°C$; ● $t = 60°C$; ▲ $t = 80°C$.

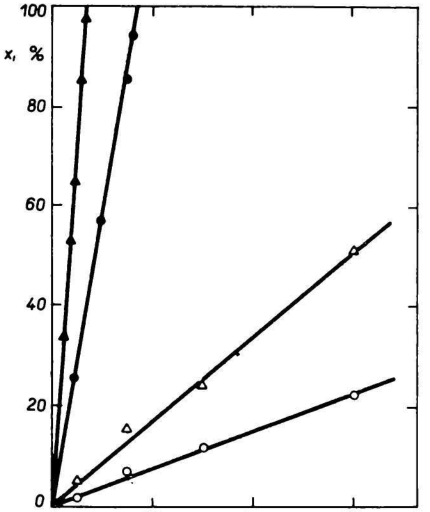


Fig. 4. Dependence of the conversion $Tl^{3+} \rightarrow Tl^+$ on the time in oxidation of 2,4,4-trimethyl-2-pentene (molar ratio olefin/Tl^{3+} 2/1, rotation speed of the stirrer 1600 rev./min).
○ $t = 20°C$; △ $t = 40°C$; ● $t = 60°C$; ▲ $t = 80°C$.

ketones and vicinal glycols were detected by spot analysis [17] and in the aqueous phase vicinal glycols were found, too. From the chromatogram of the organic phase (Fig. 2) it is evident that by the oxidation of 2,4,4-trimethyl-2-pentene a smaller assortment of oxidation products is obtained. By comparing the results of the GLC and MS analyses the ketones (peaks *2—7*) were investigated.

Influence of the parameters on the course of the reaction

Temperature

The isothermal dependences of the conversion $Tl^{3+} \rightarrow Tl^{+}$ (x) on time are plotted in Figs. 3 and 4.

The empiric starting rates were calculated from the slopes of the isotherms and the empiric activation energy was determined from the Arrhenius equation (Table 1).

Table 1

Influence of temperature on the course of the reaction
(molar ratio olefin/Tl^{3+} 2/1, rotation speed of the stirrer 1600 rev./min)

Olefi	t, °C	Empiric starting rate v mol l^{-1} s^{-1}	Empiric activation energy E^* J mol^{-1}
I	20	0.11×10^{-3}	31 800
	40	0.27×10^{-3}	
	60	0.70×10^{-3}	
	80	1.10×10^{-3}	
II	20	0.23×10^{-4}	54 500
	40	0.52×10^{-4}	
	60	4.10×10^{-4}	
	80	8.20×10^{-4}	

Table 2

Yields of products of the oxidation of trimethylpentenes by thallium(III) sulfate in aqueous medium
(data in weight %)

Olefin	t, °C	C_7 ketone	C_8 ketones	C_8 aldehyde	C_9 aldol	C_{16} aldols	C_8 glycol
I	20	11	18	3	9	53	6
	40	12	19	2	6	54	7
	60	18	23	30	4	17	8
	80	18	21	50	2	—	9
II	20		86				14
	40		85				15
	60		84				16
	80		84				16

The temperature has an influence also on the selectivity. With increasing temperature the amount of formed glycols is increased, too (Table 2). However, the temperature has a great influence on the formation of the aldolization products. It is evident (Table 2) that *e.g.* at 20°C these products represent about 50%, but at 80°C only a minor part. The suppression of the aldol condensation leads to the formation of corresponding amount of aldehyde.

Molar ratio olefin/Tl^{3+}

This dependence was studied in the range 1/1—5/1 at 20°C and at a constant rotation speed of the stirrer 1600 rev./min. It was found that the change of the olefin/Tl^{3+} ratio in the above range has no influence on the reaction rate. It has no visible effect on the selectivity of the reaction, either.

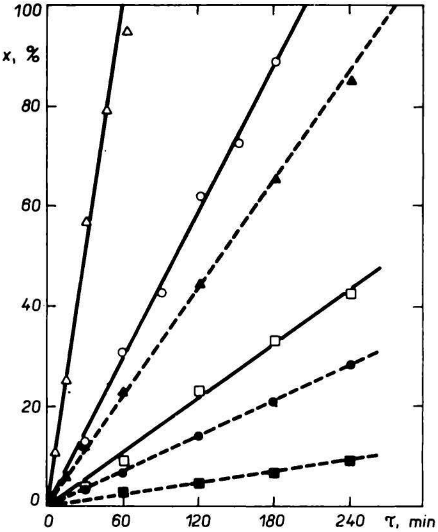


Fig. 5. Dependence of the conversion $Tl^{3+} \rightarrow Tl^{+}$ on the rotation speed of the stirrer (molar ratio olefin/Tl^{3+} 2/1).
□ $z = 1000$ rev./min; ○ $z = 1400$ rev./min; △ $z = 1600$ rev./min.
——— Oxidation of 2,4,4-trimethyl-1-pentene; – – – – oxidation of 2,4,4-trimethyl-2-pentene.

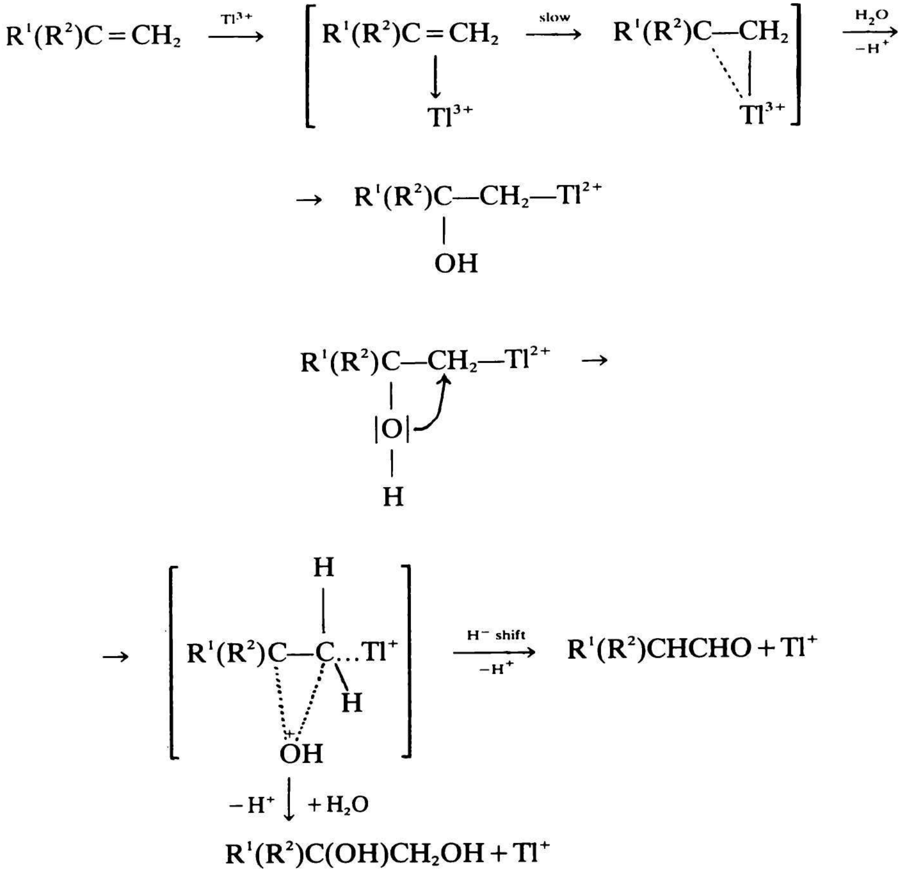
Stirring

From the dependence of the conversion rate $Tl^{3+} \rightarrow Tl^{+}$ and from the rotation speed of the stirrer (Fig. 5) it is evident that with the increasing number of rotations the reaction rate is increasing essentially.

Discussion

The oxidation of branched olefins by thallium(III) sulfate in aqueous medium takes place under the formation of carbonyl compounds and vicinal glycols. The reaction mechanism involves three steps: a) the formation of a π-complex by an electrophilic attack of the Tl^{3+} ion on the double bond; b) the change of the π-complex into a σ-complex — this being the decisive step with respect to the reaction rate [4, 5, 19]; c) the demetallization of S_N2 hydrolytic adduct – this step is decisive for the ratio of the glycol and the carbonyl (in fact those are competitive reactions).

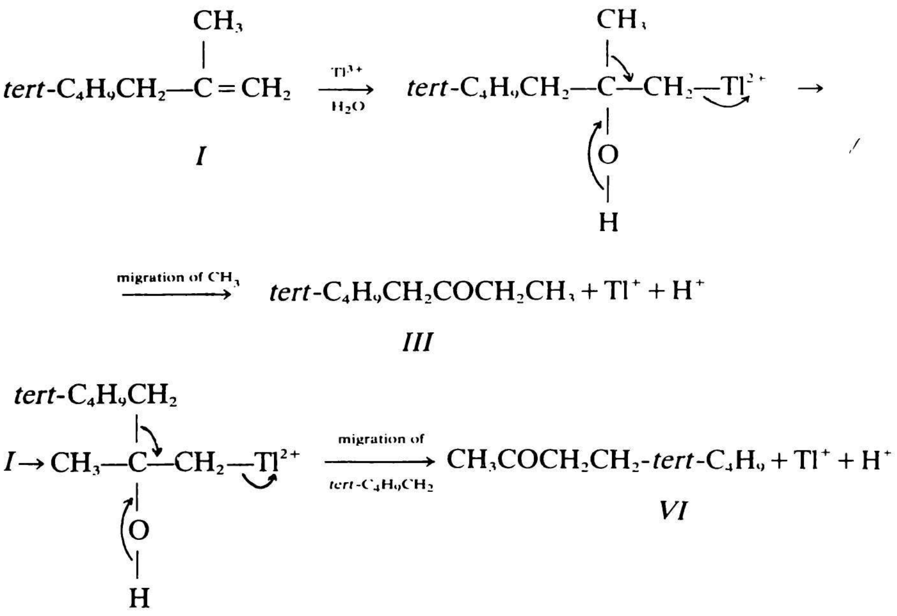
The course of this reaction is shown in Scheme 2



Scheme 2

In the oxidation of branched C_8 olefins a significant formation of isomeric ketones takes place (Table 2).

This may be explained in such a way that during the oxythallation the activated complex has more a character of a carbonium ion than *e.g.* during the oxymercurization [19]; this enables the cationotropic rearrangements leading to the formation of isomeric ketones. The formation of some isomeric ketones during the oxidation of 2,4,4-trimethyl-1-pentene is shown in Scheme 3



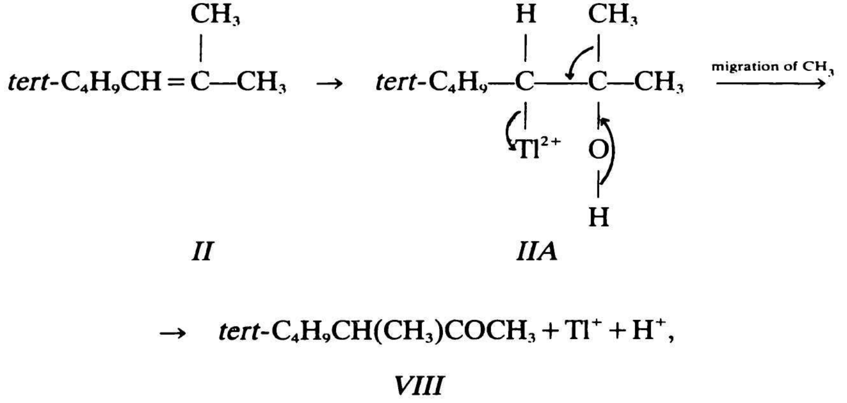
$$tert\text{-}C_4H_9CH_2{-}C(CH_3){=}CH_2 \ (I) \xrightarrow[H_2O]{Tl^{3+}} tert\text{-}C_4H_9CH_2{-}C(CH_3)(OH){-}CH_2{-}Tl^{2+} \xrightarrow{\text{migration of } CH_3} tert\text{-}C_4H_9CH_2COCH_2CH_3 \ (III) + Tl^+ + H^+$$

$$I \rightarrow CH_3{-}C(CH_2\text{-}tert\text{-}C_4H_9)(OH){-}CH_2{-}Tl^{2+} \xrightarrow[tert\text{-}C_4H_9CH_2]{\text{migration of}} CH_3COCH_2CH_2\text{-}tert\text{-}C_4H_9 \ (VI) + Tl^+ + H^+$$

Scheme 3

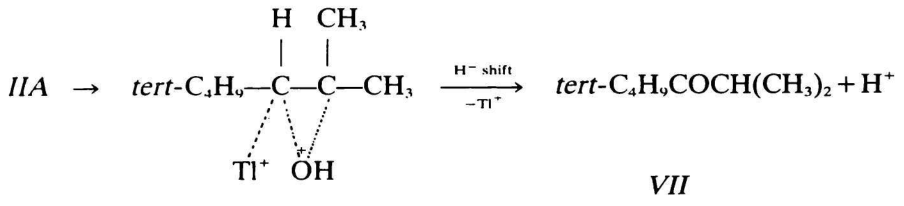
The migration ability is increasing with the size of the migrating group, *i.e.* in the sequence $CH_3 < C_2H_5 < C_3H_7 < C_4H_9 \ll C_6H_5$. The higher yield of ketone *VI* as compared with *III* (Fig. 1) can be also explained by the higher migration ability of the *tert*-butyl against the methyl group.

In the same way it is possible to illustrate also the formation of some isomeric ketones during the oxidation of 2,4,4-trimethyl-2-pentene (Scheme 4).



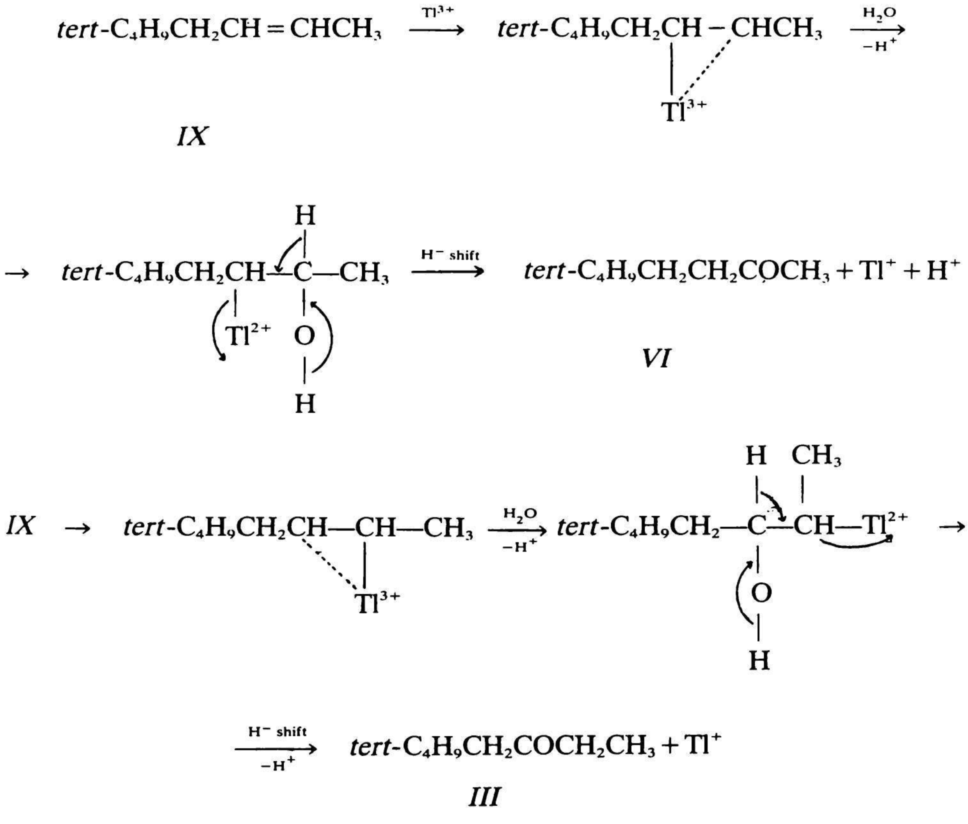
$$tert\text{-}C_4H_9CH{=}C(CH_3){-}CH_3 \ (II) \rightarrow tert\text{-}C_4H_9{-}CH(Tl^{2+}){-}C(CH_3)(OH){-}CH_3 \ (IIA) \xrightarrow{\text{migration of } CH_3}$$

$$\rightarrow tert\text{-}C_4H_9CH(CH_3)COCH_3 \ (VIII) + Tl^+ + H^+,$$



Scheme 4

This makes it possible to explain the formation of isomeric ketones *III* and *VI* during the oxidation of 2,4,4-trimethyl-2-pentene: Under the influence of hyperconjugation of *tert*-butyl in a strong acid medium there occurs evidently also the isomerization of the double bond with a consecutive rearrangement of the methyl group from C-2 to C-1, this leading to the formation of 5,5-dimethyl-2-hexene (*IX*). Ketones *III* and *VI* are probably formed by the oxidation of the latter, as shown in Scheme 5



Scheme 5

The influence of temperature on the course of the conversion of thallium(III) sulfate effected by an excess of olefins is shown in Figs. 3 and 4. The time dependence of the conversion is linear since in the given experimental conditions the reaction occurs in the diffuse region where the reaction rate depends on the diffusion of olefin into the phase of the aqueous solution of thallium(III) sulfate, where reacting olefins have a very slight solubility. This is indicated also by the course of the dependence of the conversion rate on the rotation speed of the stirrer (Fig. 5). Here, the kinetic course of the reaction has a character of a reaction of a pseudozero order. The dependence of the reaction rate on temperature is expressed as an empiric reaction rate (Table 2). The empiric activation energy is $E^* = 31\ 800\ \mathrm{J\ mol^{-1}}$ for the oxidation of 2,4,4-trimethyl-1-pentene and $E^* = 54\ 500\ \mathrm{J\ mol^{-1}}$ for the oxidation of 2,4,4-trimethyl-2-pentene. From the values in Table 1 it is evident that the reaction rate is rapidly increasing with the increasing temperature. It can be also seen that the oxidation of 2,4,4-trimethyl-2-pentene is much slower than the oxidation of 2,4,4-trimethyl-1-pentene, most probably due to the steric hindrances caused by the structure of olefin. The substituents on C-2 and C-3 hinder to some extent the admittance of the Tl^{3+} ion and thus also the formation of the oxythallium adduct. However, the influence of temperature is here more expressed than in the oxidation of 2,4,4-trimethyl-1-pentene.

The dependence of the content and composition of the products of the studied oxidation on the reaction temperature is shown in Table 2. Only components, which were present in a more significant concentration and consisting essentially of ketones and C_8 aldehyde were identified. Besides, 6 products of C_{16}, attributed to the aldolization of the oxidation products of 2,4,4-trimethyl-1-pentene, were found. Their content was evaluated approximately as a total. In a small extent a C_9 product, probably formed during the aldolization reaction of C_7 or C_8 derivatives, with the correspondent C_1 or C_2 carbonyl compounds was detected. On the other hand, in the oxidation of 2,4,4-trimethyl-2-pentene, besides vicinal glycols, only C_8 ketones are formed. The presence of products of the aldolization reaction was observed neither in the C_9 nor in the C_{16} region. This can be explained by the relatively low reactivity of ketones in comparison with aldehydes.

The formation of vicinal glycols is for 2,4,4-trimethyl-2-pentene about two times higher than for 2,4,4-trimethyl-1-pentene.

Very expressive is the dependence of the range of aldol condensation on the temperature — with the increase of the latter aldol condensation practically ceased (Table 4). This circumstance may have a considerable technical meaning and may essentially influence the economy of the process.

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