

1-Methyl-2-cyclopentylpiperidine (*IVd*)

A solution of 0.8 g of a mixture of bases, obtained by reduction of 2-cyclopentylpyridine methiodide with sodium borohydride, in 13 ml of acetic acid was hydrogenated on 13 mg of Adams catalyst. The conventional work-up of the mixture gave 0.62 g of product, b.p. 95–97°C/12 Torr, which contained 58% of the required compound and 42% of 2-cyclopentylpiperidine<sup>1</sup>. This mixture was refluxed with 2 ml of formic acid and 1 ml of 40% formaldehyde for 7 hours. The conventional work-up gave, 0.41 g of pure product, b.p. 102°C/18 Torr. For C<sub>11</sub>H<sub>21</sub>N (167.3) calculated: 79.02% C, 12.66% H, 8.32% N; found: 79.09% C, 12.73% H, 8.30% N. Compounds *Xd* and *IXd* were prepared in a similar manner.

1-Methyl-4-cyclopentyl-3-piperideine (*Xd*), b.p. 91°C/10 Torr. For C<sub>11</sub>H<sub>19</sub>N (165.3) calculated: 79.94% C, 11.59% H, 8.47% N; found: 79.95% C, 11.61% H, 8.39% N. <sup>1</sup>H-NMR spectrum (p.p.m.): N—CH<sub>3</sub> 2.43 (s), N—CH<sub>2</sub> (t; 6 Hz), N—CH<sub>2</sub>—C= 2.83–2.97 (m), CH= 5.33–5.46 (m), CH<sub>2</sub>—C= 2.0–2.26 (m), 1.20–1.90.

1-Methyl-4-cyclopentylpiperidine (*IXd*), b.p. 96°C/10 Torr. For C<sub>11</sub>H<sub>21</sub>N (167.3) calculated: 79.02% C, 12.66% H, 8.32% N; found: 79.15% C, 12.68% H, 8.26% N.

Dehydration of 1-Methyl-4-(1-hydroxy-2-propyl)piperidine (*IXa*)

Thionyl chloride (3.64 g, *i.e.* 0.03 mol) in diethyl ether (20 ml) was added to a solution of *IXa* (ref.<sup>8</sup>) (3.92 g, 0.025 mol) in diethyl ether (110 ml) and the mixture stirred at room temperature for 20 minutes. After decomposition with 5 ml of water 10 ml of a 40% sodium hydroxide solution were added and the mixture extracted with diethyl ether. The solvent was distilled off, leaving a mixture of substances, b.p. 68–71°C/10 Torr (2.18 g, 63%). Using GLC (preheater 140°C, column 120°C, flow 150 ml of nitrogen/min) the following compounds were isolated:

1-Methyl-4-isopropenylpiperidine (*IXe*), b.p. 60.5–61.5°C/10 Torr (57%). For C<sub>9</sub>H<sub>17</sub>N (139.2) calculated: 77.63% C, 12.30% H, 10.06% N; found: 77.50% C, 12.49% H, 10.02% N. IR spectrum: (values of characteristic bands only):  $\gamma$ (=C—H) 890 vs,  $\nu$ (C=C) 1644 s,  $\nu$ (=CH<sub>2</sub>)<sub>as</sub> 3075 m (in cm<sup>-1</sup>). <sup>1</sup>H-NMR spectrum (p.p.m.): CH<sub>3</sub>—N 1.07 (s), CH<sub>e</sub>—N 1.64–1.94 (m), CH<sub>2</sub>= 3.55 (m), other 0.62.

1-Methyl-4-isopropylidenepiperidine (*IXg*), b.p. 66–67.5°C/10 Torr (43%). For C<sub>9</sub>H<sub>17</sub>N (139.2) calculated: 77.63% C, 12.30% H, 10.06% N; found: 77.79% C, 12.43% H, 10.26% N. <sup>1</sup>H-NMR spectrum (p.p.m.): CH<sub>3</sub>—C 1.55 (s), CH<sub>3</sub>—N 2.17 (s), other 2.25.

1-Methyl-3-(1-hydroxy-2-propyl)piperidine (*VIa*)

A solution of 127 g of methyl iodide in 60 ml of methanol was added to a solution of 54.3 g of 3-pyridyldimethylmethanol<sup>9</sup> in 125 ml of methanol and the mixture refluxed for 22 hours. After evaporation 105.4 g (92%) of crude methiodide of 3-pyridyldimethylmethanol were obtained, which was dissolved in 260 ml of water and additioned with 16.5 g of sodium hydroxide dissolved in 260 ml of water and a solution of 16.5 g of sodium borohydride in 130 ml of water. The mixture was stirred under a reflux condenser at room temperature for one hour, then extracted with chloroform, and the extract dried over potassium carbonate. After evaporation of the solvent 42.7 g (76%) of a mixture of reduced amino alcohols were obtained, b.p. 106–109°C/11 Torr, which was hydrogenated in 600 ml of ethanol on 1.28 g of Adams catalyst. From the hydrogenation experiment 33.4 g (77%) of *VIa* were obtained, b.p. 106–108°C/12 Torr. The product was purified by GLC (preheater 150°C, column 130°C, flow of nitrogen 200 ml/min); b.p. 107 to 108°C/14 Torr, m.p. 39–40.5°C. For C<sub>9</sub>H<sub>19</sub>NO (157.25) calculated: 68.74% C, 12.18% H,

8.91% N; found: 68.69% C, 12.28% H, 8.82% N.  $^1\text{H-NMR}$  spectrum (p.p.m.):  $\text{CH}_3\text{-C}$  1.12 (s),  $\text{CH}_3\text{-N}$  2.23 (s),  $\text{N-CH}_2\text{CH}_2\text{-CH}_2$  2.62–2.86 (m),  $\text{N-CH}_2\text{CH}_2\text{-CH}$  2.86–3.08 (m), other 1.35–2.03.

#### Dehydration of 1-Methyl-3-(1-hydroxy-2-propyl)piperidine (VIa)

The reaction was carried out analogously as dehydration of IXa. A mixture of substances with b.p. 78–94°C/10 Torr (65% yield) was thus obtained which was submitted to GLC (preheater 155°C, column 130°C, nitrogen flow 135 ml/min) to give:

1-Methyl-3-isopropenylpiperidine (VIe), b.p. 78–79°C/10 Torr (69%). For  $\text{C}_9\text{H}_{17}\text{N}$  (139.2) calculated: 77.63% C, 12.30% H, 10.06% N; found: 77.50% C, 12.45% H, 9.96% N.  $^1\text{H-NMR}$  spectrum (p.p.m.):  $\text{CH}_3\text{-C}$  1.70 (bs),  $\text{CH}_3\text{-N}$  2.23 (s),  $\text{CH}_2\text{-N}$  2.65–3.10 (m),  $\text{CH}_2\text{=}$  4.68 (m), other 1.55–2.55.

1-Methyl-3-isopropylidenepiperidine (VIg), b.p. 85–86°C/10 Torr (31%). For  $\text{C}_9\text{H}_{17}\text{N}$  (139.2) calculated: 77.63% C, 12.30% H, 10.06% N; found: 77.38% C, 12.25% H, 10.30% N.  $^1\text{H-NMR}$  spectrum (p.p.m.):  $\text{CH}_3\text{-C}$  1.65 (s) and 1.66 (s),  $\text{CH}_3\text{-N}$  2.24 (s),  $\text{CH}_2\text{-CH}_2\text{H}_a\text{-N}$  2.6–2.8 (m),  $\text{=CH}_2\text{-N}$  2.90 (m), other 1.80–2.52.

The analyses were carried out in the analytical laboratories of our Department (head Dr L. Helešic) and the measurement of  $^1\text{H-NMR}$  spectra was carried out under the direction of Dr P. Trška.

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## OXIDATION OF METHYLPENTENES BY THALLIUM(III) SULFATE

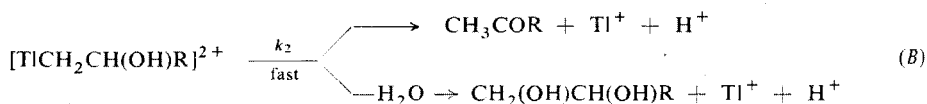
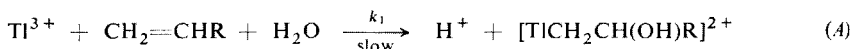
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Kinetics of oxidation of methylpentenes by thallium (III) sulfate in aqueous medium has been followed by UV spectrophotometry and its activation parameters have been determined. The effect of concentration of hydrogen ions and of ionic strength on the oxidation rate has been studied: the oxidation rate has been found to increase with increasing concentration of hydrogen ions and to decrease with increasing ionic strength. The effect of structure of the methylpentenes on the distribution of the products has also been examined.

Oxidation of alkenes by solutions of thallic salts has been intensively studied from point of view of preparative organic chemistry as well as from theoretical aspects<sup>1-13</sup>. As the solvent served usually water<sup>1,2,5,12,14</sup>, methanol<sup>4,15,17</sup> and acetic acid<sup>9,16</sup>. The kinetic behaviour of lower alkenes (C<sub>2</sub> to C<sub>4</sub>) during their reaction with thallic salts along with the distribution of the oxidation products are described in the fundamental studies of Henry<sup>12,16</sup>. In aqueous medium, two characteristic products are formed by the oxidation of alkenes, *viz.* a carbonyl compound (an aldehyde or a ketone) and a vicinal diol. The formation of these products as well as the kinetics has been explained by a generally adopted mechanism, whose principal features are shown in equations (A) and (B).



The step determining the reaction rate is the formation of the intermediate hydroxythallation adduct according to Eq. (A). The assumption that the formation of the intermediate adduct occurs as one step of the reaction is substantiated by the fact that the adduct could be isolated under favourable conditions<sup>3,7</sup>. In addition, a spectral proof of the formation of the hydroxythallation adduct during the oxidation of alkenes in aqueous medium has been also presented<sup>12</sup>.

## EXPERIMENTAL

*Kinetic methods.* The kinetics of oxidation of methylpentenes was followed spectrophotometrically by measuring the decrease of absorbance accounted for by the decrease of concentration of the  $\text{TI}^{3+}$  ions. The reaction rates with reaction halfives lower than 15 s were determined by

applying the "stopped-flow" method on a spectrophotometer Durrum-Gibson D-110, whereas slower reactions were followed on a spectrophotometer VSU-2-P (Zeiss, Jena). The reaction temperature was kept at a chosen value within the limits of  $\pm 0.1^\circ\text{C}$ . For all experiments, during which the temperature was variable, the concentration of the free sulfuric acid was 0.05 mol/l. The standard temperature of  $25^\circ\text{C}$  was maintained during experiments with variable concentration of sulfuric acid or of lithium sulfate.

**Materials.** The solution of thallium(III) sulfate was prepared as described previously<sup>18</sup>. The concentration of thallium was determined by two independent methods, *viz.* titration<sup>19</sup> of  $\text{Tl}^+$  with a titrant solution of  $\text{KIO}_3$ , and titration<sup>20</sup> of iodine liberated by the reaction of  $\text{Tl}^{3+}$  with KI, with a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ .

2-Methyl-1-pentene (*I*) (chromatographic purity min 99.9%) was prepared by pyrolysis of acetate of 2-methyl-1-pentanol<sup>21</sup>. 4-Methyl-1-pentene (*II*) (chromatographic purity min. 99.0%) was prepared by the same method<sup>21</sup> from 4-methyl-2-pentanol acetate (W. Pieck Chemical Works, Nováky). 2-Methyl-2-pentene (*III*) (chromatographic purity min. 99.9%) was obtained by isomerization of the compound *II* in the presence of  $\text{PdCl}_2$  as a catalyst<sup>22</sup> and subsequent rectification of the mixture of isomeric methylpentenes.

The other chemical used were commercial products, reagent grade purity, of Lachema, Brno.

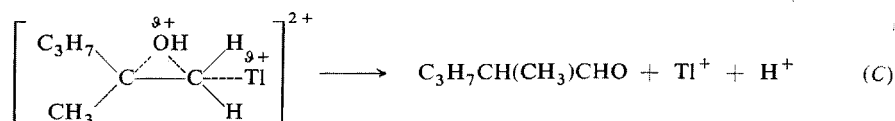
**Analysis of the reaction mixture.** The glycols obtained were determined by the periodate method<sup>23</sup>. For the identification of the oxidation products and finding their distribution, four methylpentenes were oxidized using a relatively high initial concentration of thallium(III) sulfate. The standard reaction conditions were as follows: 250 ml of thallium(III) sulfate ( $[\text{Tl}^{3+}] = 0.33$  mol/l), 20 ml of the alkene (approx. one-mol excess over  $\text{Tl}^{3+}$ ),  $[\text{H}_2\text{SO}_4]/[\text{Tl}_2(\text{SO}_4)_3] = 4$ ,  $t = 25^\circ\text{C}$ . The procedure has been described in the previous work<sup>18</sup>. For the determination of the content of organic products, gas chromatography was employed. The products of oxidation of the compounds *II* and *III* were analyzed on an instrument Fractovap 2300 (Carlo Erba, Milan) with a flame ionization detector. The column, length 2.5 m and diameter 2 mm, contained 10% polyethylene glycol adipate on chromatone. Working temperature was  $70^\circ\text{C}$ , input pressure of  $\text{N}_2$  1.5 atm, flow rates of  $\text{N}_2$ ,  $\text{H}_2$ , and air were 35, 85, and 85 ml/min, respectively. In the case of the substances *IV* and *II* the separation was not complete, therefore an apparatus Chrom II (Laboratorní přístroje, Prague) with a capillary column, 50 m long, packed with squalane, was used for their gas chromatographic analysis. The working conditions were as follows: temperature of the column  $75^\circ\text{C}$ , overpressure of  $\text{N}_2$  1.06 atp, flow rate of  $\text{H}_2$  50 ml/min. For the determination of methyl isobutyl ketone and ethyl isopropyl ketone in the reaction products, methyl ethyl ketone was used as the internal standard. The yields of the organic substances from the oxidation of the compound *I* were determined from the areas of their peaks in the chromatographic record of the product. The ketones were identified by gas chromatography applying the addition of the corresponding standards. The oxidation products from the substance *I* were identified from mass spectra obtained by the GCMS method on an instrument MAT 111 GNOM (Varian). The chromatograph was equipped with a packing column (length 1 m, diameter 3 mm). Working conditions: column temperature  $35^\circ\text{C}$ , flow rate of He 13 ml/min, energy of electrons 80 eV, intensity 270 mA, temperature of the ion source  $200^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Oxidation of the first three isomeric methylpentenes (Table I) by an aqueous solution of thallium(III) sulfate in the presence of free sulfuric acid leads to the formation of two characteristic products: one of them is always a vicinal glycol with preserved

structure of the skeleton of the starting alkene, the other product is a carbonyl compound (an aldehyde or a ketone) whose nature depends on the structure of the alkene.

As can be seen from Table I, the yields of the two products are in the limits of experimental errors almost quantitative. The only exception is the oxidation of the compound *I*, where the situation is slightly more complicated: we found small amounts of other substances, too, in the reaction mixture, *viz.* 2-pentanone (1.6%), 3-hexanone (4.2%), and 2-methyl-2-pentanol. Our explanation of the formation of 3-hexanone is based on the general reaction mechanism, where the intermediate hydroxythallation adduct can be decomposed in two alternative ways: decomposition involving the migration of hydrogen with the participation of the neighbouring hydroxyl group,



or decomposition with the migration of the methyl group,

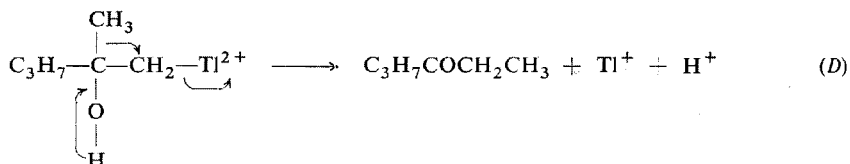


TABLE I

Distribution of the Oxidation Products at 25°C

Alkene	Carbonyl product (yield, %) <sup>a</sup>	Vicinal glycol (yield, %) <sup>a</sup>
2-Methyl-1-pentene ( <i>I</i> )	2-methylpentanal (26.6) <sup>b</sup>	2-methyl-1,2-pentanediol (65.3)
2-Methyl-2-pentene ( <i>II</i> )	2-methyl-3-pentanone (80.2)	2-methyl-2,3-pentanediol (18.8)
4-Methyl-1-pentene ( <i>III</i> )	4-methyl-2-pentanone (82.0)	4-methyl-1,2-pentanediol (13.0)
4-Methyl-2-pentene ( <i>IV</i> )	4-methyl-2-pentanone + 2-methyl-3-pentanone (83.8)	4-methyl-2,3-pentanediol (13.5)

<sup>a</sup> With respect to the  $\text{Ti}^{3+}$  reacted; <sup>b</sup> 2-pentanone (yield approx. 1.6%), hexanone (4.2%), and 2-methyl-2-pentanol are additional products.

TABLE II  
Activation Parameters of Oxidation of Methylpentenes

Pentene	$H^\ddagger$ , kJ/mol	$S^\ddagger$ , J/mol. deg
2-Methyl-1	43.1	-45.6
2-Methyl-2	33.1	-69.5
4-Methyl-1	34.3	-112.6

The ratio of the yields of 2-methylpentanal (decomposition C) and 3-hexanone (decomposition D) obtained indicated that the probability of the former scheme of decomposition is much higher, which proves a higher migration capacity of hydrogen as compared with the methyl group.

The formation of 2-pentanone can result from the oxidation decomposition of the hydroxythallation complex, as found previously<sup>18</sup>. The presence of 2-methyl-2-pentanol in the reaction mixture is explained by the hydration of 2-methyl-1-pentene under catalytic action of sulfuric acid, whose occurrence has been proved experimentally also in the absence of a thallium salt. Although a concentration of  $H_2SO_4$

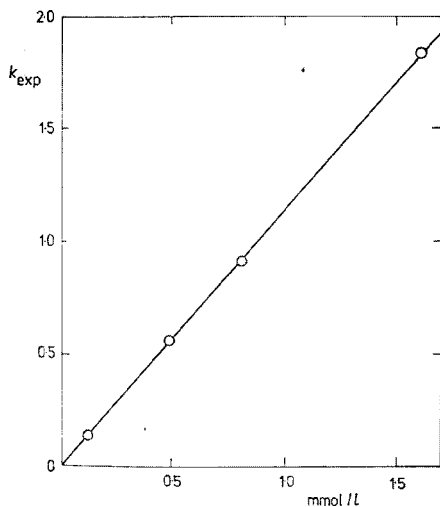


FIG. 1

Dependence of  $k_{exp}$  on the Concentration of 2-Methyl-1-pentene (I) at 25°C

Concentration of sulfuric acid 0.05 mol/l.

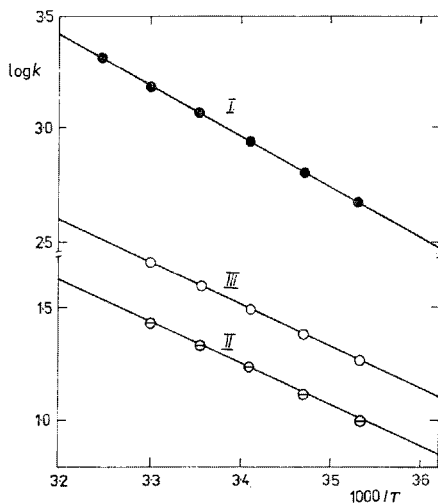


FIG. 2

Dependence of the Rate of Oxidation of the Methylpentenes I-III on Temperature

of at least 50% in the aqueous solution is known to be necessary for the hydration of alkenes branched at the double bond, the hydration effect observed could be explained in the system in question by the extraction effect of the olefinic phase present.

*Kinetic study.* For the kinetic study we used the technique, which has been successfully applied during the investigation of other alkenic substrates<sup>12,24</sup>. We found the oxidation rates for the three isomeric methylpentenes to be in accordance with the kinetic equation of second order,

$$-d[\text{Ti}^{3+}]/dt = -d[\text{alkene}]/dt = k_{11}[\text{Ti}^{3+}][\text{alkene}]. \quad (1)$$

Since all the measurements were performed with a high excess of the alkene, the reaction order decreased — the kinetic behaviour observed could be described by the kinetic equation of pseudo-first order,

$$-d[\text{Ti}^{3+}]/[\text{Ti}^{3+}] dt = -d \ln [\text{Ti}^{3+}]/dt = k_1[\text{alkene}] = k_{\text{exp}}. \quad (2)$$

The values of  $k_{\text{exp}}$  were plotted *versus* the concentration of the alkene (Fig. 1). The linear form of this dependence also proves the direct proportionality of the reaction rate to the first power of the alkene concentration. The same reaction order was found for the other isomers as well.

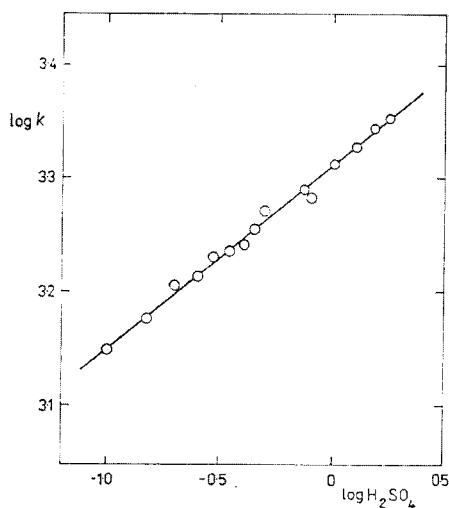


FIG. 3

Effect of the Concentration of Sulfuric Acid on the Rate of Oxidation of 2-Methyl-1-pentene (I) at 25°C

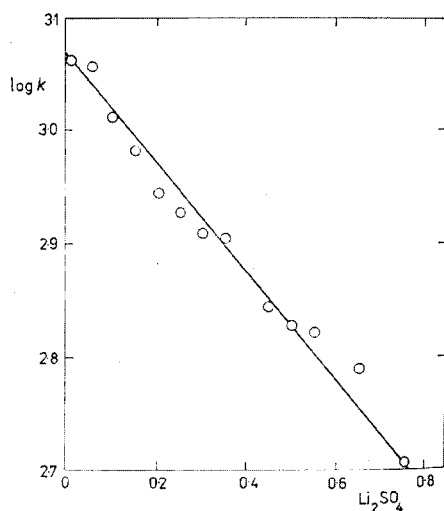


FIG. 4

Effect of the Concentration of Lithium Sulfate on the Rate of Oxidation of 2-Methyl-1-pentene (I) at 25°C

The kinetic measurements were carried out using concentrations appropriate for the spectral technique, *i.e.* with the concentration of the thallium(III) ion  $2.5 \cdot 10^{-5}$  to  $1.0 \cdot 10^{-4}$  mol/l and that of the alkene  $2.5 \cdot 10^{-4}$  to  $2.0 \cdot 10^{-3}$  mol/l. The concentration of sulfuric acid was 0.05 mol/l in all cases except when the dependence of the reaction rate on that concentration was examined.

*Dependence of the reaction rate on the temperature.* The changes of the reaction rate with varying temperature were followed in the range of 10–30°C. The dependence found for the three methylpentenes is plotted in Fig. 2. The activation parameters calculated from this dependence are given in Table II.

*Salt effects* were investigated during the oxidation of 2-methyl-1-pentene in two series of experiments: we examined on one hand the effect of free sulfuric acid and on the other hand the effect of concentration of a neutral electrolyte ( $\text{Li}_2\text{SO}_4$ ) with a constant concentration of free  $\text{H}_2\text{SO}_4$  in the oxidizing solution. In the first series we varied the concentration of free  $\text{H}_2\text{SO}_4$  from 0.05 to 1.75 mol/l. The dependence of the rate constant of second order on the concentration of  $\text{H}_2\text{SO}_4$  is plotted (in the logarithmic scale) in Fig. 3. In the second series we followed the change of the oxidation rate due to the addition of lithium sulfate in the concentration span of 0.05 to 0.65 mol/l with the constant concentration of  $\text{H}_2\text{SO}_4$ , 0.05 mol/l. The dependence of the 2nd order rate constant on the concentration of  $\text{Li}_2\text{SO}_4$  is shown in Fig. 4.

From the plots of rate constants of oxidation of 2-methyl-1-pentene *vs* concentrations of the electrolytes added, the significance of the salt effects is apparent. In the first case the reaction rate increases with increasing concentration of sulfuric acid (Fig. 3), in the second case an increase of the concentration of the neutral electrolyte  $\text{Li}_2\text{SO}_4$  depresses the reaction rate (Fig. 4). The salt effects found are in agreement with the observations of Henry<sup>1</sup>, who reports an increase of the reaction rate of oxidation of ethylene by thallic salts, when the concentration of free mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ) increased. An addition of  $\text{NaClO}_4$  led also to a speeding-up of the oxidation of ethylene by thallium(III) perchlorate. Henry discussed all these changes based on the decrease of activity of water in the oxidation solution, due to the increasing concentration of the electrolyte. The decrease of activity of water brings about an activation of the  $\text{Tl}^{3+}$  ion resulting in an enhanced reaction rate. This concept is supported by the fact that an analogous increase of reaction rate was observed during some oxidations of unsaturated organic molecules by  $\text{Hg}^{2+}$  ions, which are isoelectronic with  $\text{Tl}^{3+}$ , in aqueous medium<sup>25,26</sup>. Henry did not discuss, however, the drop of the oxidation rate of ethylene due to an increase of concentration of sodium sulfate.

We assume the decrease of the rate of oxidation of 2-methyl-1-pentene by thallium(III) sulfate in the presence of lithium sulfate to be due to the formation of sulfato-thallation complexes, whose detailed composition is not known. The formation of these complexes competes then with the oxidation of the alkene and results in the



deactivation of thallic ions. A detailed analysis of this problem requires an additional study, which would provide us with data on the relative stability of sulfothallic or also olefinic complexes with the  $Tl^{3+}$  ion.

To this assumption we are led by the analogy with the oxidation of olefins by  $PdCl_2$  in aqueous medium, where the overall oxidation rate is lowered when the concentration of the chloride ions increases, on account of the formation of various chloropalladium complexes<sup>27</sup>. A direct comparison of the two reactions, however, is not possible, because in the medium of chloride ions, insoluble complexes of thallium(I) chlorothallates are formed and the reaction is completely inhibited.

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