

## OXIDATION OF INNER ALKENES BY THALLIC SULPHATE IN AN AQUEOUS MEDIUM

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The kinetics of oxidation of inner alkenes (endoalkenes) by thallic sulphate in an aqueous medium have been investigated by UV spectrophotometry and the activation parameters have been determined. The effects of temperature, alkene structure and acidity of the medium on the course of the reaction were investigated. The main reaction products were found to be ketones and the corresponding vicinal diols.

In the last five years increasing attention has been paid to the oxidation of alkenes by thallic salts. A valuable contribution to preparative organic chemistry are the works of McKillop and coworkers<sup>1-3</sup>, who developed preparation of aldehydes and ketones by one-step oxidation of alkenes with thallic nitrate in methanol. The first paper dealing with the kinetics of oxidation of lower (C<sub>2</sub> to C<sub>4</sub>) alkenes by thallic salts was published by Henry<sup>4</sup>. Byrd and Halpern<sup>5</sup> extended Henry's kinetical studies to the oxidation of alkenols by Tl<sup>3+</sup> ions in an aqueous solution of perchloric acid. All these studies were done on low-molecular-weight alkenes and alkenols.

Our attention has been focussed on the oxidation of some inner alkenes by thallic sulphate in aqueous sulphuric acid. The effects of the fundamental experimental parameters on the reaction rate and on distribution of the products have been investigated.

### EXPERIMENTAL

*Materials.* A solution of thallic sulphate in aqueous sulphuric acid was prepared as previously described<sup>6</sup>. Concentration of thallium was determined iodometrically<sup>7</sup>.

2-Methyl-2-pentene (*I*, chromatographic purity  $\geq 99.9\%$ ), *trans*-4-methyl-2-pentene (*trans-II*) and *cis*-4-methyl-2-pentene (*cis-II*), both of chromatographic purity  $\geq 99\%$ , were prepared as previously described<sup>8,9</sup>. 2,4,4-Trimethyl-2-pentane (*III*), chromatographic purity  $\geq 99.5\%$ , was synthesized according to<sup>6</sup>. The other chemicals were of A. G. purity (Lachema, Brno).

*Kinetic methods.* The oxidation kinetics of inner alkenes were followed spectrophotometrically in the UV region<sup>5,9</sup>. The courses of the reactions with half-times below 30 s were followed by the "stopped-flow" method in a spectrophotometer Durrum-Gibson D-110 (Durrum Instruments, Palo Alto, California). Slower reactions were followed with a spectrophotometer VSU-2-P

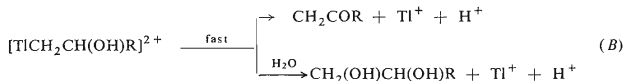
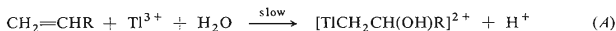
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(Zeiss, Jena, G.D.R.). The reaction temperatures, covering a range from 25 to 40°C, were maintained with a precision of  $\pm 0.1^\circ\text{C}$ . In all experiments with temperature as the variable the concentration of free sulphuric acid was 0.05M. Experiments investigating the effect of concentration of sulphuric acid were all carried out at a temperature of 25°C.

*Analysis.* The glycols obtained were determined quantitatively by the periodate method<sup>10</sup>. For the sake of identification and determination of distribution of the oxidation products the oxidation of inner alkenes was carried out at a relatively high concentration of thallic sulphate, as described earlier<sup>6</sup>. The standard conditions were: 150 ml of  $\text{Ti}_2(\text{SO}_4)_3$ ,  $[\text{Ti}^{3+}] = 0.322$  gram-ions per liter, 20 ml of an alkene and molarity of sulphuric acid 1.415. The organic oxidation products were quantitated by GC-MS analysis using the method described elsewhere<sup>6,9</sup>.

## RESULTS AND DISCUSSION

Oxidation of alkenes by thallic sulphate in an aqueous medium of free sulphuric acid gave rise to two characteristic products. One, invariably, was a vicinal diol, with the carbon skeleton of the starting alkene, the other was a ketone whose structure was given by that of the starting alkene. The essential features of the process can be described by reactions (A) and (B)



The rate-controlling step is the formation of the hydroxythallic adduct (reaction (A)), demonstrated by spectral analysis<sup>5</sup>. The distribution of oxidation products of inner alkenes in relation to the reaction temperature is shown in Fig. 1.

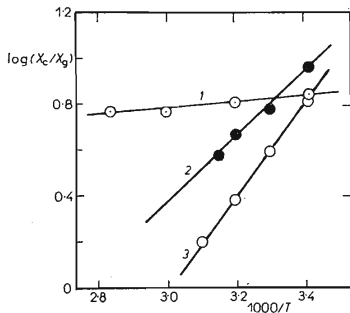
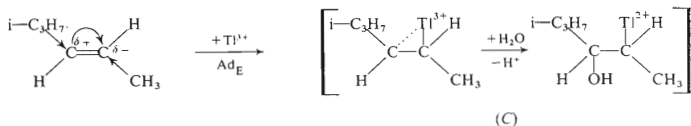


FIG. 1  
Effect of Temperature on Distribution of Oxidation Products  
1 2,4,4-trimethyl-2-pentene (III), 2 *trans*-4-methyl-2-pentene (*trans*-II), 3 2-Methyl-2-pentene (I).

The simplest case is the oxidation of 2-methyl-2-pentene (*I*), producing 2-methyl-3-pentanone (*IV*); oxidation of the other olefins took a more complex course.

The formation of two products in the oxidation of *trans*-4-methyl-2-pentene (*trans*-*II*) can be explained by statistical probabilities of the attack of a water molecule on C<sub>2</sub> (producing 4-methyl-2-pentanone, *V*) and on C<sub>3</sub> (leading to 2-methyl-3-pentanone, *IV*). The ratio of *IV* to *V* increased with increasing temperature (Table I).

A possible explanation of the prevalence of *IV* over *V* seems to be the stronger +I-effect of the isopropyl group, which activates the C<sub>3</sub> atom, compared to the +I-effect of the methyl group, activating the C<sub>2</sub> atom. Thus the formation of the hydroxythallic adduct (reaction Ad<sub>E</sub>) should favour the ketone *IV* (reaction (C)).



The oxidation of 2,4,4-trimethyl-2-pentene (*III*) gave a mixture of ketones. The mechanism of their formation is discussed in our recent paper<sup>6</sup>.

Fig. 1 shows that with increasing temperature the quantity of the glycol rose at the expense of the ketone. This was most marked in the oxidation of 2-methyl-2-pentene (*I*), whereas with 2,4,4-trimethyl-2-pentene (*III*) the dependence on temperature was negligible.

The distribution of the oxidation products is controlled by decomposition of the hydroxythallic adduct (*B*): the nucleophilic attack of water, leading to a glycol with the simultaneous cleavage of the C—Ti bond, competes with migration of H<sup>-</sup>, giving rise to a ketone. The proportion of the two reactions is temperature-dependent<sup>6,11</sup>.

TABLE I

Proportion of Ketones *IV* and *V* Formed in Oxidation of *trans*-4-Methyl-2-pentene in Relation to Temperature

°C	Ratio of <i>IV</i> to <i>V</i>	°C	Ratio of <i>IV</i> to <i>V</i>
20	2·20	40	3·63
30	3·02	45	3·91

Assuming that the two reactions are of an equal order in respect to the intermediary hydroxythallic adduct, the ratio of  $k_k$  (formation of ketone) to  $k_g$  (formation of glycol) will equal the ratio or the mole fraction  $X_k$  (ketone) to  $X_g$  (glycol).  $\log(X_k/X_g)$  vs  $1/T$  is plotted in Fig. 1. The values of  $\Delta \Delta H^\ddagger$  and  $\Delta \Delta S^\ddagger$  calculated from this graph are given in Table II.

*Kinetic measurements.* The kinetics were investigated by the method that had proved useful in studying the oxidation of other alkenes by metallic ions<sup>5,9</sup>. The oxidation rate of inner alkenes was found to obey the second-order kinetic equation:

$$-d[\text{Tl}^{3+}]/dt = -d[\text{alken}]/dt = k[\text{Tl}^{3+}][\text{alken}]. \quad (1)$$

The excess of an alkene was sufficient in all experiments to reduce the reaction order by one degree. Therefore, the kinetic data obtained should fit the pseudo-first-order kinetic equation.

$$-d[\text{Tl}^{3+}]/[\text{Tl}^{3+}] dt = -d \ln [\text{Tl}^{3+}]/dt = k[\text{alken}] = k_{\text{exp}}. \quad (2)$$

TABLE II

Values of  $\Delta \Delta H^\ddagger$  and  $\Delta \Delta S^\ddagger$  for Oxidation of Inner Alkenes (Reaction (B))

Alkene	$\Delta \Delta H^\ddagger$ , kJ	$\Delta \Delta S^\ddagger$ , J/mol deg
I	-13.48	-84
<i>trans</i> -II	-16.78	-38
III	-16.04	42

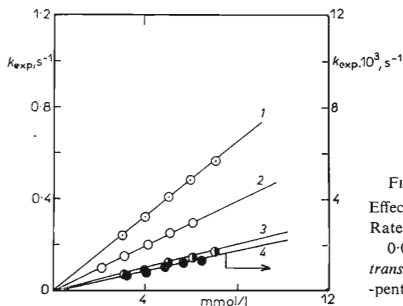


FIG. 2  
Effect of Alkene Concentration on Reaction Rate at 25°C

0.05M-H<sub>2</sub>SO<sub>4</sub>; 1 2-methyl-2-pentene, 2 *trans*-4-methyl-2-pentene, 3 *cis*-4-methyl-2-pentene, 4 2,4,4-trimethyl-2-pentene.

The dependence of  $k_{\text{exp}}$  on concentration of an alkene (Fig. 2) justifies this equation. The kinetic measurements were performed at concentrations suitable for the spectral method:  $2.5 \cdot 10^{-5}$  to  $2.0 \cdot 10^{-4}$  gram-ion of  $\text{Tl}^{3+}/\text{l}$ , alkene molarity  $2.5 \cdot 10^{-4}$  to  $2.0 \cdot 10^{-2}$ . The molarity of free sulphuric acid was 0.05 in all experiments excepting those in which the effect of sulphuric acid concentration on the reaction rate was studied.

*Effect of temperature on the reaction rate.* The change in reaction rate with increasing temperature was investigated in the range 25 to 40°C. The activation parameters, calculated from the dependence of  $\log k$  (second-order rate constant) on  $1/T$  by the least-square method, are given in Table III. They show the considerable effect of an alkene structure on the oxidation rate. Important factors will be steric hindrance (reducing the reaction rate) and the rather high activation enthalpy in the case of 2,4,4-trimethyl-2-pentene (III).

TABLE III  
Second-Order Rate Constants at 25°C and Activation Parameters of Oxidation of Inner Alkenes

Alkene	$k$ , l/mol s	$\Delta H^\ddagger$ , kJ/mol	$\Delta S^\ddagger$ , J/mol deg
I	$49.60 \pm 0.35$	$29.13 \pm 0.88$	$-25 \pm 1.9$
<i>trans</i> -II	$81.90 \pm 0.57$	$21.66 \pm 0.54$	$-30 \pm 3.1$
<i>cis</i> -II	$23.80 \pm 0.17$	$36.79 \pm 0.84$	$-21 \pm 1.7$
III	$2.14 \pm 0.01$	$54.97 \pm 0.93$	$-13 \pm 1.7$

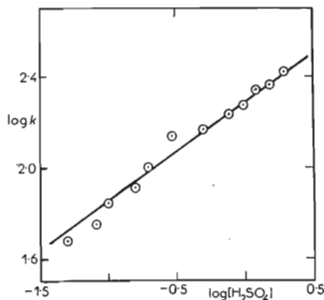


FIG. 3  
Effect of Concentration of Free Sulphuric Acid on the Oxidation Rate of 2-Methyl-2-pentene at 25°C ( $k$  in l/mol s)

*Effect of concentration of H<sup>+</sup> ions on the reaction rate.* This was investigated with 2-methyl-2-pentene (I) at 25°C. Molarity of free sulphuric acid ranged from 0.05 to 2.00. The second-order rate constant as a logarithmic function of concentration of sulphuric acid is plotted in Fig. 3; it shows that the reaction rate increases with the increasing concentration of the acid. This observation is in agreement with Henry's in the oxidation of ethylene by thallic salts and ours in the oxidation of methylpentenes by thallic sulphate<sup>9</sup>, the phenomenon was discussed therein<sup>9</sup>.

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