SEMIEMPIRICAL RELATIONS BETWEEN STRUCTURE AND REACTIVITY FOR THE OXIDATION OF ALKENES BY THALLIUM(III) SULFATE IN AQUEOUS MEDIUM

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Kinetics of oxidation of alkenes by aqueous solution of thallium (III) sulfate in the presence of sulfuric acid has been investigated by UV spectrophotometry. The experimental rate constants have been determined for oxidations of various alkenes. The reactivity of the olefins has been related to their structure by employing the Taft's equation.

Kinetic behaviour of lower alkenes $(C_2$ to $C_4)$ in their reaction with thallic salts and the distribution of the reaction products have been studied first by Henry[1]. In our preceding paper[2] we have followed the kinetics of oxidation of methylpentenes by thallium(III) sulfate in aqueous medium and determined the rate constants k_{exp} for the individual methylpentenes. In that work we have also suggested the principal features of the oxidation mechanism.

EXPERIMENTAL

Kinetic measurements. The kinetics of oxidation of alkenes by an aqueous solution of thallium-(III) sulfate in the presence of sulfuric acid was followed by UV spectrophotometry: absorbance changes in the range of $200-240$ nm, associated with the decrease of concentration of Tl^{3+} ions resulting from their reduction by the alkene substrate, were measured. A spectrophotometer VSU 2-P (Zeiss, Jena) with thermostatted cells was used. The reaction temperature was kept at 25°C within the limits of ± 0.1°C. The standard concentration of free sulfuric acid was 0·05 mol/l $(I = 0.15)$ in all cases.

Materials. A solution of thallium(III) sulfate was prepared as described previously[3]. 4-Methyl--1-pentene (chromatographic purity 99·0%) was prepared by pyrolysis of 4-methyl-2-pentanol acetate[4] with the successive rectification of the formed mixture of 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene. 1-Hexene, 1-heptene, and 1-octene were obtained from commercial chemicals by rectification, until chromatographic purity was attained. All other chemicals were commercial products, reagent grade purity (Lachema, Brno).

RESULTS AND DISCUSSION

The generally adopted mechanism of oxidation of alkenes by thallic salts in aqueous medium assumes that in the rate-determining step, an intermediate hydroxythallation adduct is formed by the electrophilic attack of the double bond of the alkene substrate by the thallic ion. For an electrophilic addition, the hydroxythallation rate can be expected to be raised by electron donor substituents (alkyl groups) and depressed by electron acceptor substituents. In order to verify this assumption we tested the effect of structure of the alkene substrates upon the reaction rate of their oxidation.

We followed the kinetics of oxidation of alkenes by thallium(III) sulfate in aqueous medium of sulfuric acid spectrophotometrically in the UV region[5]. The oxidation rates for all the alkenes studied obey the kinetic equation of 2nd order. This 2nd order was lowered by one by using a sufficient excess of the alkene, so that the kinetic behaviour of the system studied could be expressed by the kinetic equation of pseudo-first

TABLE I

Values of the Apparent Rate Constants of Oxidation of Substituted Ethylenes at 25°C

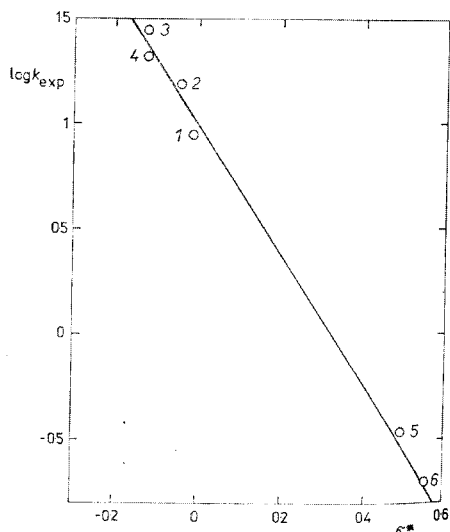| Alkene	k, mol^{-1} l s^{-1}	Alkene	k, mol^{-1} l s^{-1}
1-Hexene	28·6	1-Octene	9·0
4-Methyl-1-pentene	21·3	Allyl alcohol	0·2
1-Heptene	15·5		

FIG. 1

Dependence of Reactivity on the Structure of Alkenes for Their Oxidation by Thallium-(III) Sulfate at 25°C

1 1-Octene, *2* 1-heptene, *3* 1-hexene, *4* 4-methyl-1-pentene, *5* ethylene, *6* allyl alcohol.

order, as verified in the preceding work[2]. The measurements were carried out with the concentrations $[Tl^{3+}]_0 = 2.5 . 10^{-5}$ to $1.0 . 10^{-4}$ mol/l, $[alkene]_0 = 2.5 . 10^{-4}$ to $2.0 . 10^{-3}$ mol/l, and $[H_2SO_4] = 0.05$ mol/l ($\mu = 0.15$). The rate constants found for a series of substituted ethylenes are given in Table I.

We tested the relation between the structure and reactivity and found an excellent correlation between log $k(RCH=CH_2)$ and Taft's σ^* parameters for R (correlation coefficient $r_{xy} = 0.94$). The values of the parameters were taken from[6].

The slope of the plot log k vs σ_R (Fig. 1) is $\sigma^* = -3.02 \pm 0.27$, which indicates that in the transition state of the reaction, the positive charge is highly localized at the carbon atom (approaching thus in its nature the carbonium ion), to which the substituent R is attached:

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{Tl}{C}}{}^{(+)}\!\!-R$$
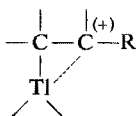
A similar correlation has been found for the oxidation of alkenols by thallium(III) perchlorate in aqueous medium[5], with $\sigma^* = -3.2$. The concept concerning the nature of the transition state occurring during the oxidation of thallic ions is, in addition, supported by the character of the analogous reaction between mercuric ions (Hg^{2+} is isoelectronic with Tl^{3+}) and alkenes in water, resulting in stable hydroxymercuration adducts. For this reaction, Tinker[7] found an excellent correlation between the reactivity of the alkene and its structure ($\sigma^* = -3.3$), which again is in accordance with the idea of the transition state with a character approaching that of the carbonium ion. A completely free (open) carbonium ion, however, can be ruled out for the hydroxymercuration, as the *cis-trans* isomerization of internal olefins, such as that of *cis*- or *trans*-butene[8] or *cis*-stilbene[9], has not been observed during that reaction.

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