ENTHALPY–ENTROPY RELATIONSHIP IN THE OXIDATION OF ALKENES BY SOLUTIONS OF THALLIC SALTS*
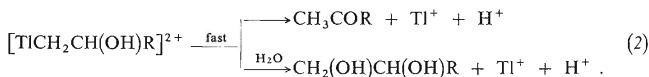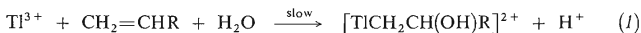
M.STRAŠÁK** and M.HRUŠOVSKÝ

Department of Organic Technology,
Slovak Institute of Technology, 880 37 Bratislava

The oxidation of alkenes by thallium(III) sulfate in aqueous medium has been studied from point of view of the enthalpy–entropy relationship. It is found that the isokinetic relationship is fulfilled in this case. Because the Taft equation is valid for one temperature it has to be valid at different temperature hence.

Several workers have previously described the oxidations of olefines by thallium(III) salts[1-7]. The kinetics and products of the oxidation of alkenes by Tl(III) in aqueous acid solutions have been interpreted by Henry[1] in terms of the following mechanism:

$$Tl^{3+} + CH_2=CHR + H_2O \xrightarrow{\text{slow}} [TlCH_2CH(OH)R]^{2+} + H^+ \quad (1)$$

$$[TlCH_2CH(OH)R]^{2+} \xrightarrow{\text{fast}} \begin{array}{l} \longrightarrow CH_3COR + Tl^+ + H^+ \\ \xrightarrow{H_2O} CH_2(OH)CH(OH)R + Tl^+ + H^+ \end{array} \quad (2)$$

The oxidation rates for alkenes are in accordance with the kinetic equation of the second-order:

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

Kinetic evidence indicates that the formation of the organo-thallic intermediate is rate-determining step[2,8]. In our recent work[9] we reported the determination of polar, steric, and resonance effects in the oxidation of alkenes by solutions of thallic salts. We showed that the rates of oxidation are satisfactorily fitted by Taft equation for the combined polar and steric effects.

In the present work the simple method is used for verification of the enthalpy–entropy relationship in the oxidation of alkenes by thallium(III) sulfate in aqueous sulfuric acid.

EXPERIMENTAL

Materials

The preparation and the purification of the alkenes, which were also used in our earlier kinetic studies, has already been described[9]. No impurities were detectable by glc. The stock solution of thallium(III) sulfate was prepared as described previously[10]. The concentration of thallium(III) was determined by two independent methods which yielded consistent results, namely *a)* by titration of iodine released by the reaction of Tl^{3+} with KI with a standard solution of $Na_2S_2O_3$ (ref.[11]), and *b)* by UV spectrophotometry[12]. The other chemicals used were comercial products of a reagent grade purity (Lachema, Brno). Redistilled water was used for the preparation of all solutions.

Kinetic Measurements

The kinetics of oxidation of alkenes by the aqueous solution of thallium(III) sulfate was followed by UV spectrophotometrically in the wavelength range of 200—240 nm by measuring the decrease of absorbance caused by the decrease of concentration of the Tl^{3+} ions. The kinetic measurements were caried out using concentrations appropriate to the spectral technique, *i.e.* with the concentration of Tl^{3+} ions $2\cdot5 \cdot 10^{-5}$—$2\cdot0 \cdot 10^{-4}$ mol/l. and that of the alkene $2\cdot5 \cdot 10^{-4}$ to $2\cdot0 \cdot 10^{-3}$ mol/l. The concentration of sulfuric acid was 0·05 mol/l ($\mu = 0\cdot15$M) in all cases. The rates of reaction with half-lives less than 30 s were determined by applying the stopped-flow method on a spectrophotometer Durrum–Gibson D-110, while the rates of slower reactions were measured in a spectrophotometer VSU-2-P (Zeiss, Jena). The reaction temperature was kept at a chosen value within the limite of $\pm0\cdot1°C$.

RESULTS AND DISCUSSION

The linear relationship between activation enthalpy and activation entropy in a series of related reactions,

$$\Delta H^* = \Delta H^0 + \beta \, \Delta S^* \tag{4}$$

is called isokinetic relationship (IKR) and is of fundamental importance in structure – reactivity correlations[13,14]. Since the quantities ΔH^* and ΔS^* are derived from experimental rate constant k then the assumption of a linear relation between them implies also validity of a linear relation between $\log k$ at two different temperatures[15,16]:

$$\log k_2 = \text{const} + K \log k_1 , \tag{5}$$

where $K = (T_2 - \beta) \, T_1/(T_1 - \beta) \, T_2$ for $T_2 > T_1$.

TABLE I

The Changes of the Rate Constants of the Second Order with Varying Temperature and Activation Parameters of Oxidation of Alkenes by Thallium(III) Sulfate in Aqueous Sulfuric Acid

k, l mol^{-1} s^{-1}					$\Delta H^{\neq}$, kcal/mol^a	$\Delta S^{\neq}$, e.u.^{a}
25°C	30°C	35°C	40°C	50°C		
	1 styrene					
1·160	1·600	2·522	4·493	7·934	9·7 ± 0·4	−23 ± 0·2
	2 allyl alcohol					
0·250	0·835	1·170	2·223	2·300	15·4 ± 0·5	− 8 ± 0·2
	3 1-hexene					
25·7	34·9	51·3	66·4	—	10·4 ± 0·2	−22 ± 0·4
	4 1-heptene					
14·9	19·2	22·5	28·5	—	7·4 ± 0·2	−32 ± 0·4
	5 1-octene					
8·40	11·97	16·22	24·83	—	7·2 ± 0·2	−29 ± 0·4
	6 4-methyl-1-pentene					
19·8	26·5	30·4	39·4	—	7·8 ± 0·2	−22 ± 0·4
	7 1-nonene					
2·3	2·9	3·5	4·4	—	9·1 ± 0·2	−25 ± 0·4
	8 1-decene					
2·5	3·2	4·5	5·5	—	9·0 ± 0·2	−25 ± 0·4
	9 1-undecene					
3·4	4·5	5·8	7·6	—	9·2 ± 0·2	−23 ± 0·4
	10 1-dodecene					
1·5	2·4	3·7	4·4	—	15·1 ± 0·3	− 5 ± 0·4
	11 1-tridecene					
0·214	0·29	0·44	0·52	—	10·9 ± 0·2	−23 ± 0·4
	12 1-tetradecene					
0·39	0·44	0·59	0·80	—	7·9 ± 0·2	−32 ± 0·4
	13 1-pentadecene					
0·49	0·62	0·79	1·08	—	7·8 ± 0·2	−32 ± 0·4
	14 1-hexadecene					
0·23	0·32	0·46	0·63	—	11·5 ± 0·2	−21 ± 0·4
	15 2-methyl-2-pentene					
49·6	63·2	76·4	93·8	—	7·0 ± 0·2	−25 ± 0·5

TABLE I
(Continued)

	k, l mol^{-1} s^{-1}				$\Delta H^{\neq}$, kcal/mol^a	$\Delta S^{\neq}$, e.u.^{a}
25°C	30°C	35°C	40°C	50°C		
	16 *trans*-4-methyl-2-pentene					
81·9	92·8	99·1	131·5	—	5·2 ± 0·1	−30 ± 0·7
	17 *cis*-4-methyl-2-pentene					
23·8	28·3	35·0	56·3	—	8·8 ± 0·2	−21 ± 0·4
	18 2,4,4-trimethyl-2-pentene					
2·14	3·21	4·69	6·75	—	13·1 ± 0·3	−13 ± 0·4
	19 2-methyl-1-pentene					
27·8	35·5	46·3	59·5	—	9·0 ± 0·2	−20 ± 0·4
	20 2,4,4-trimethyl-1-pentene					
13·0	16·1	20·0	24·5	—	6·7 ± 0·2	−33 ± 0·4
	21 2-ethyl-1-hexene					
22·0	27·4	—	39·0	54·0^b	5·9 ± 0·1	−31 ± 0·2
	22 α-methylstyrene					
1·79	2·05	2·63	3·02	4·20	6·6 ± 0·1	−36 ± 0·2

^{a} Error calculated according to [18]; ^{b} At 60°C $k = 74\cdot0$ l mol^{-1} s^{-1}.

This relation has been used by us for verification of validity of equation (4) since the values of k at different temperatures are mutually independent and their possible error is approximately known.

For the kinetic study we used technique which has been succesfully applied during the investigation of other alkenic substrates[3,17]. These reactions exhibited second-order kinetics corresponding to the rate law defined by Eq. (3). 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 equation of pseudo-first-order:

$$-d[Tl^{3+}]/[Tl^{3+}] \, dt = -d \ln [Tl^{3+}]/dt = k[\text{alkene}] = k_{obs}. \qquad (6)$$

The values of k_{obs} were plotted *versus* the concentration of a source RCH=CH$_2$ alkenes in Fig. 1. The linear form of these 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 alkenes as well.

The changes of the reaction rate with varying temperature are listed in Table I together with the activation parameters calculated from this dependence.

Kinetic data of oxidation of these alkenes are depicted in Fig. 2.

We tested the relation between the rate constants and found an excellent correlation for their (correlation coefficient $r_{xy} = 0.982$). The slope of the plot log k_{40} vs log k_{25} is $K = 0.900$. Then if follows from definition of that for calculation of isokinetic temperature: $\beta = 572$ K. According to Hinshelwood[19] who distinguishes three cases of the mutual relation of activation parameters in a series of related reactions, is $K < T_1/T_2$ and $\beta > T_2$. The oxidation of alkenes by thallium(III) sulfate in aqueous sulfuric acid is, in this manner, the case where both activation parameters are variable in the sense that their effects partially compensate each other.

From Fig. 2 it is obvious that the isokinetic relationship is fulfilled in the oxidation of alkenes by thallium(III) sulfate. This is the condition for validity of Taft equation at different temperatures if the Taft equation is valid for one temperature.
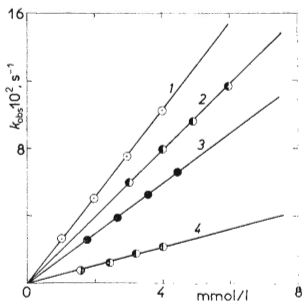

FIG. 1

Dependence of k_{obs} on the Concentration of Alkenes at 25°C

Concentration of sulfuric acid 0.05 mol/l. Concentration of Tl^{3+} ions $1.0 \cdot 10^{-4}$ mol/l. *1* 1-Hexene, *2* 4-methyl-1-pentene, *3* 1-heptene, *4* 1-octene.
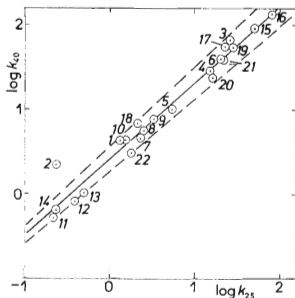
FIG. 2

Kinetic Data of Oxidation of Alkenes by Thallium(III) Sulfate in Aqueous Sulfuric Acid

Full line corresponds to real regression line for the whole series, dashed lines to 99% interval of reliability calculated from Student t-test. Number at points correspond to the alkenes in Table I.

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