

OXIDATION OF ALKENES $R^1R^2C=CH_2$ BY THALLIC SULPHATE IN AN AQUEOUS MEDIUMM. STRAŠÁK^a,* M. HRUŠOVSKÝ^a, J. URBANEC^a, Š. HOLOTÍK^b and J. VOJTKO^a^a Department of Organic Technology, and^b Laboratory of Mass Spectrometry,
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Using spectrophotometry in the UV region, the kinetics of oxidation of C_2 -branched terminal alkenes by thallic sulphate in aqueous sulphuric acid have been investigated and the activation parameters of the individual alkenes have been determined. The effects of temperature, alkene structure and hydrogen ion concentration on the reaction course were also assessed. The oxidation rate increased with increasing concentration of hydrogen ions. The main reaction products were aldehydes, ketones and vicinal glycols. An increase in temperature raised the yield of carbonyl compounds at the expense of glycols. The ratio of rate constants for the formation of isomeric ketones, k_1 (migration of R^1) to k_2 (migration of R^2), can be correlated with the Taft polar constants by the equation $\log(k_2/k_1) = \rho^*(\sigma_2^* - \sigma_1^*)$, where $\rho^* = -3.7$. This suggests that the more electron-releasing group migrates more readily.

Oxidation of alkenes by $Tl(III)$ salts has, in recent years, been attracting more attention, both from the theoretical and the preparative points of view. The attention, however, has been paid mainly to oxidation of $RCH=CH_2$ alkenes¹⁻⁶ or cycloalkenes⁷⁻⁹. Oxidation of alkenes $R^1R^2C=CH_2$ has so far been treated in few papers^{10,11} and is, therefore, dealt with in the present communication.

EXPERIMENTAL

Materials: A solution of thallic sulphate was prepared as previously described¹². The thallium concentration was determined by titrating the iodine liberated by reaction of Tl^{3+} with KJ with a defined solution of $Na_2S_2O_3$ (ref.¹³). 2-Methyl-1-pentene (*I*), chromatographic purity 99.9%, was obtained¹⁴ by pyrolysis of 2-methyl-1-pentanol acetate. 2,4,4-Trimethyl-1-pentene (*II*), chromatographic purity 99.6%, was obtained by distillation and efficient rectification¹² from diisobutylene, supplied by CHZJD, Nat. Corp. Bratislava. 2-Ethyl-1-hexene (*III*), chromatographic purity 99.8%, was prepared by pyrolysis at 570°C of 2-ethylhexyl acetate, obtained by acetylation of 2-ethyl-1-hexanol (CHZ ČSSP, Záluží) with acetic anhydride. 2-Methyl-1-butene (*IV*), chromatographic purity 99.6%, was obtained by pyrolysis at 480°C of 2-methyl-1-butanol acetate, prepared by acetylation of 2-methyl-1-butanol (Fluka) with acetic anhydride. α -Methyl-

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styrene (*V*), chromatographic purity 99.9%, was obtained by distillation of the crude product from Slovnaft, Nat. Corp., Bratislava.

Standards GC-MS. The respective vicinal diols were prepared¹⁵ by oxidation of alkenes by a catalytic amount of OsO_4 in anhydrous tert-butyl alcohol. 2-Methylbutanal, 2-ethylhexanal, 2-octanone and 2-hexanone were prepared by oxidation of 2-methyl-1-butanol, 2-ethyl-1-hexanol, 2-octanol and 2-hexanol, respectively, with sodium dichromate using a modification of a published method¹⁵. 2-Methyl-3-pentanone was prepared by pyrolysis of a mixture of barium isobutyrate and barium propionate, followed by rectification of the crude product. The other chemicals were commercial A.G. products (Lachema, Brno).

Analysis of the oxidation products. To identify the oxidation products and determine their proportion the experiments were carried out at a relatively high initial concentration of thallic sulphate; the standard conditions were: 150 ml of a solution of $Tl_2(SO_4)_3$, conc. 0.370 gram-ion Tl^{3+}/l , 20 ml of an alkene (C_8 and α -methylstyrene) or 10 ml of an alkene (C_5 and C_6) i.e. about 2 molecules of an alkene per Tl^{3+} ion, 1.254M- H_2SO_4 . The procedure was described in a preceding paper¹². The glycols formed were determined quantitatively by the periodate method¹⁶. The other organic products were determined by the GC-MS analysis.

Gas chromatography. The oxidation products of 2-methyl-1-butene, 2-methyl-1-pentene and 2-ethyl-1-hexene were determined with an apparatus Chrom II (Laboratory Instruments, Prague) with a capillary column 50 m long, packed with SE, and a flame ionization detector (sensitivity 1/10). A constant temperature of 90°C (oxidation of *I* and *IV*) or 140°C (oxidation of *III*) was maintained. The flow rates of the gases were: H_2 25 ml/min, air 11 ml/min; the pressure of N_2 was 1.1 atm. The oxidation products of compound *II* were determined with the apparatus Fractovap 2300 (Carlo Erba, Milano) by a method described elsewhere¹². (In that communication¹² the non-identified peak δ in Fig. 1 was assigned later to 2,4,4-trimethyl-2-pentanol). The oxidation products of α -methylstyrene (*V*) were identified with an apparatus Hewlett Packard 5830A using a column 1.5 m long packed with SE-coated (3%) Chromaton NAW-DMC, a flame ionization detector, flow rate 15 ml N_2 /min, a constant temperature of 140°C; the temperature of the feed was 194°C.

Mass spectrometry. An apparatus MAT 111 Gnom (Varian) with a 3 m column packed with SE-coated (3%) Chromosorb WHP was used. The feed temperature was 190°C, the temperature programme (8°C/min) was in the range 80–300°C. The temperature of the ion source was 225°C, the flow rate of He 15 ml/min, ionization voltage 80 eV, current intensity 270 mA. The spectra of the individual samples were compared with those of authentic compounds.

Kinetic methods. The kinetics of oxidation of alkenes $R^1R^2C=CH_2$ by aqueous thallic sulphate in the presence of sulphuric acid were followed by UV spectrophotometry in the region 200–240 nm. The courses of the reactions with half-times shorter than 30 s were followed by the "stopped-flow" method with a spectrophotometer Durrum-Gibson D-110 (Palo Alto, California). The slower reactions were followed with a spectrophotometer VSU-2-P (Zeiss, Jena). The reaction temperature was maintained with a precision of $\pm 0.1^\circ C$. In all experiments with temperature as the variable the concentration of sulphuric acid was 0.05 mol/l. The experiments at different concentrations of the acid were all performed at 25°C.

RESULTS AND DISCUSSION

Effects of Temperature and Alkene Structure on Relative Contents of the Products

The oxidation of alkenes $R^1R^2C=CH_2$ gives rise to a more complex mixture of products than the oxidation of alkenes $RCH=CH_2$. These are aldehyde *VI* and the

isomeric ketones VII, VIII, as a result of migration of substituents R_1 and R_2 , and the vicinal glycol IX, with the preserved carbon skeleton of the starting alkene^{11,12}.

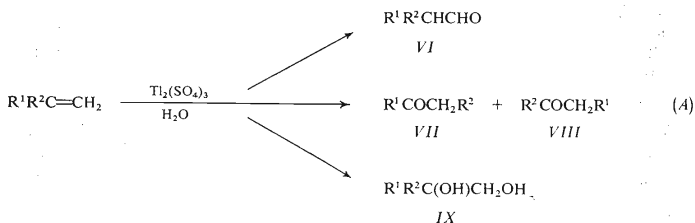


TABLE I

Effect of Temperature on Distribution of the Products (in mole fractions) in the Oxidation of 2-Methyl-1-butene

Temperature °C	C ₄ ketone ^a	C ₅ ketones	C ₅ aldehyde	C ₅ glycol	C ₅ alcohol
10	0.028	0.301	0.231	0.402	0.038
15	0.047	0.304	0.238	0.386	0.025
20	0.046	0.312	0.250	0.375	0.017
30	0.034	0.346	0.284	0.328	0.008

^a 2-Butanone was formed.

TABLE II

Effect of Temperature on Distribution of the Products (in mole fractions) in the Oxidation of 2-Methyl-1-pentene

Temperature °C	C ₅ ketone ^a	C ₆ ketones	C ₆ aldehyde	C ₆ glycol	C ₆ alcohol
10	0.069	0.054	0.197	0.617	0.063
20	0.075	0.057	0.217	0.610	0.041
30	0.076	0.061	0.251	0.549	0.063
40	0.084	0.072	0.270	0.528	0.046

^a 2-Pentanone was formed.

TABLE III

Effect of Temperature on Distribution of the Products (in mole fractions) in the Oxidation of C_8 Alkenes

Temperature °C	C_7 ketone ^a	C_8 ketones	C_8 aldehyde	C_8 glycol	C_8 alcohol	C_9 aldol	C_{16} aldols
compound II							
20	0.170	0.203	0.041	0.073	0.047	0.100	0.366
40	0.186	0.209	0.028	0.085	0.052	0.067	0.373
60	0.220	0.218	0.326	0.076	0.032	0.035	0.093
80	0.201	0.218	0.496	0.069	0.010	0.006	—
compound III							
20	0.038	0.308	0.286	0.313		0.050	—
40	0.049	0.351	0.297	0.254	traces	0.048	—
60	0.070	0.366	0.349	0.183		0.029	—
80	0.117	0.366	0.345	0.150		0.020	—

^a 4,4-Dimethyl-2-pentanone or 4,4-dimethyl-3-heptanone was formed.

TABLE IV

Effect of Temperature on Distribution of the Products (in mole fractions) in the Oxidation of α -Methylstyrene

Temperature °C	Acetophenone	Benzyl methyl ketone	2-Phenyl-1,2-propandiol
20	0.066	0.605	0.329
40	0.082	0.662	0.256
60	0.098	0.699	0.203
80	0.087	0.739	0.174

The oxidation products and their yields (based on reacted Tl^{3+}) in relation to temperature are given in Tables I–IV. From Tables I–III it is apparent that in the oxidation of a terminal alkene substituted on C_2 the formation of the corresponding aldehyde (VI) is considerable and markedly depends on temperature (increases with increasing temperature). Its mechanism may be as follows:

TABLE V

Relative Migration Properties of Alkyl Groups in the Oxidation of Alkenes $R^1R^2C=CH_2$ by $Tl_2(SO_4)_3$ in Water at 20°C

R^1	R^2	k_2/k_1	R^1	R^2	k_2/k_1
CH ₃	CH ₃	1.00	C ₂ H ₅	C ₂ H ₅	1.00
CH ₃	C ₂ H ₅	2.29	C ₂ H ₅	CH ₃	0.44
CH ₃	n-C ₃ H ₇	2.60	C ₂ H ₅	n-C ₄ H ₉	1.35
CH ₃	neo-C ₅ H ₁₁	4.33			

Fig. 1 shows that the ratio of rate constants for the formation of the isomeric ketones, k_2/k_1 , is related to the Taft polar constants²⁰, σ^* , by the equation $\log(k_2/k_1) = \rho^*(\sigma_1^* - \sigma_2^*)$ where $\rho^* = -3.7$. This suggests that the group with a stronger electron-releasing tendency will migrate more readily. The relatively high negative value of ρ^* demonstrates that the transitive form, produced by the migration, has more or less the character of a carbonium ion. In the oxidation of alkenes $R^1R^2C=CH_2$ by $Tl(NO_3)_3$ in methanol¹¹ the value of ρ^* was found to be -4 .

In the oxidation of α -methylstyrene (Table IV) no formation of the corresponding aldehyde or ethyl phenyl ketone (the latter would be formed by migration of the methyl group) was observed. This fact suggests that the phenyl group migrates much more readily than an alkyl group (in analogy to Wagner-Meerwein's rearrangement). Similar results were obtained in the oxidation of α -methylstyrene by $Tl(NO_3)_3$ in methanol²¹.

The presence of the C₄, C₅ or C₇ ketone (Tables I–III) indicates that the oxidation of alkenes by Tl^{3+} in aqueous sulphuric acid was accompanied to some extent

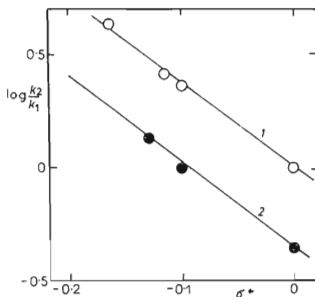


FIG. 1

Ratio of Rate Constants of the Formation of Isomeric Ketones, k_2 (migration of R^2) to k_1 (migration of R^1), in Relation to Alkene Structure at 20°C, ($\sigma^* = \sigma_2^* - \sigma_1^*$, $\rho^* = -3.7$)

1 Migration of a substituent in respect to CH₃ (correlation coefficient 0.998), 2 migration of a substituent in respect to C₂H₅ (correlation coefficient 0.999).

by oxidative fragmentation^{10,12}. The formation of acetophenone (*V*) can also be explained as due to this fragmentation. The produced formaldehyde and aldehyde can undergo aldol self-condensation or (in the case of substituents with high +I-effects) intercondensation (Table III).

The presence of 2-methyl-2-butanol, 2-methyl-2-pentanol and 2,4,4-trimethyl-2-pentanol after oxidation of compounds *IV*, *I* and *III* respectively (Tables I and II) and the trace of 2-ethyl-2-hexanol or dimethylphenylcarbinol after oxidation of com-

TABLE VI
Second-Order Rate Constants and Activation Parameters of the Oxidation of Alkenes
 $R^1R^2C=CH_2$

Alkene	$k, l \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger, \text{ kJ/mol}$	$\Delta S^\ddagger, \text{ J mol}^{-1} \text{ K}^{-1}$
<i>I</i>	27.8 ± 0.19	37.7 ± 0.7	-83.7 ± 1.7
<i>II</i>	13.0 ± 0.09	28.1 ± 0.6	-138.2 ± 1.7
<i>III</i>	22.0 ± 0.15	25.2 ± 0.5	-129.8 ± 0.7
<i>V</i>	1.79 ± 0.0125	27.6 ± 0.5	-150.7 ± 1.0

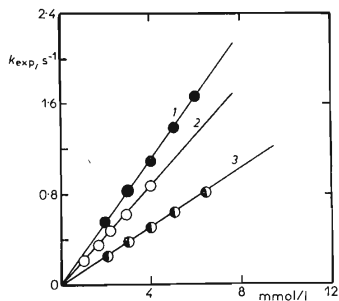


FIG. 2
Effect of Olefin Concentration on k_{exp} at 25°C, concentration of H_2SO_4 0.05 mol/l
1 2-Methyl-1-pentene (*I*), 2 2,4,4-trimethyl-1-pentene (*II*), 3 2-ethyl-1-hexene (*III*).

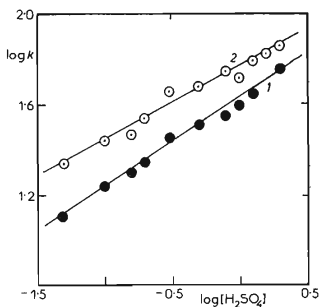


FIG. 3
Effect of Concentration of H_2SO_4 on Oxidation Rate at 25°C
1 2,4,4-Trimethyl-1-pentene (*II*), 2 ethyl-1-hexene (*III*).

pounds *III* or *V* may be due to hydration of the alkenes catalysed by sulphuric acid. A similar phenomenon was observed even in the absence of thallium. Hydration at a lower concentration of H_2SO_4 than the usual 50% (w./w.) may be caused by an extraction effect of the present olefinic phase.

Tables I–IV show that with increasing temperature the total yield of carbonyl compounds increases while the yield of a glycol decreases. This is a significant difference from the oxidation of inner alkenes by Tl^{3+} , in which, by contrast, the yield of carboxyl compounds (ketones) decreases with increasing temperature²².

Kinetic Measurements

The kinetics of the oxidation were followed by the method successfully used in studying the oxidation of other alkenes by Tl^{3+} (refs.^{5,8,22,23}). The oxidation rate of terminal alkenes substituted on the C_2 atom obeys the second-order kinetic equation¹:

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

All the kinetic measurements were performed at a sufficient excess of the alkenes, at which the reaction order was one degree lower. The kinetics could then be described by the pseudo-first-order kinetic equation:

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

Fig. 2, showing the dependence of k_{exp} on concentration of an alkene, justifies use of equation (2).

The kinetic measurements were carried out at concentrations suitable for the spectral method: $2.5 \cdot 10^{-5}$ to $5.0 \cdot 10^{-4}$ gram-ion Tl^{3+}/l , $2.5 \cdot 10^{-4}$ to $2.0 \cdot 10^{-2}$ mol alkene/l, 0.05M- H_2SO_4 (excepting experiments in which the effect of concentration of H_2SO_4 was investigated).

The reaction rate as a function of temperature was investigated in the range 25–50°C. In the coordinates of the Arrhenius equation straight lines were obtained. Activation parameters calculated from these lines are given in Table VI.

The effect of hydrogen ion concentration was examined on compounds *II* and *III* at 25°C. Concentration of free sulphuric acid ranged from 0.05 to 2.00 mol/l. The second order rate constant in relation to concentration of the acid is plotted in logarithmic coordinates in Fig. 3; it shows an increase in the oxidation rate with increasing concentration of the acid. The same phenomenon was observed by Henry¹ in the oxidation of ethylene by thallic salts and by us in the oxidation of methylpentenes²³ and inner alkenes²¹ by aqueous $Tl_2(NO_3)_3$ (see the discussions therein).

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