Tetrahedron Letters No. 50, pp 5037 - 5040.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/1208-5037$02.00/0

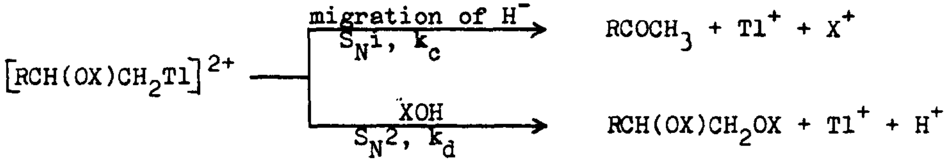
MEDIUM AND SUBSTITUENT EFFECTS ON THE SELECTIVITY OF THE OXIDATION OF TERMINAL N-ALKENES BY THALLIC SALTS[1]

Milan Strašák* and Jaroslav Majer

Department of Analytical Chemistry, Pharmaceutical Faculty, Comenius University,
880 34 Bratislava, Czechoslovakia

In earlier papers of this series we showed that oxidation of alkenes by solutions of thallic salts suit Taft´s equation and isokinetic relationship, too [2 - 4]. We studied the enthalpy-entropy relationship in this reaction and we found that the oxidation of alkenes by thallic salts was a case where both activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) were variable in the sense that their effects partially compensated each other[3].

Water and methanol are frequently used as a reaction medium for the oxidation of alkenes by thallic salts[5]. The second stage of this reaction corresponds to a dethallation step and formation of the final oxidation products:



where X = H or R

This is the case when a compound satisfying the structural assumption for a given empirical relationship undergoes two competitive reactions of the same order to the intermediate oxythallation adduct. Then, according to absolute rate theory[6], the ratio of the amounts of both products X_c/X_d is independent of time and equal to the ratio of the two kinetic constants k_c/k_d.

$$\log(X_c/X_d) = \log(k_c/k_d) = (\rho_c^* - \rho_d^*)\sigma^* + \log(k_c^{\circ}/k_d^{\circ})$$

This paper concerns itself with the examination of the response of selectivity to changes in substituents and solvent polarity for a series of monosubstituted ethylenes. The selectivity data are listed in the Tables I and II and are illustrated in Figure[7].

Table I. Substituent Effects on the Selectivity of the Oxidation of $RCH=CH_2$ Alkenes by Thallium(III) Perchlorate at 20°C

Substituent	Mol fraction		$\delta_R \Delta G^{\ddagger a}$
	Ketone	Diol	
H^b	0.435	0.565	0.64
$CH_3{}^c$	0.640	0.360	-1.40
$C_2H_5{}^b$	0.705	0.295	-2.13
$n\text{-}C_4H_9$	0.919	0.081	-5.93
$n\text{-}C_5H_{11}$	0.701	0.299	-2.08
$n\text{-}C_6H_{13}$	0.758	0.242	-2.79
$i\text{-}C_4H_9$	0.649	0.351	-1.52
$n\text{-}C_7H_{15}$	0.773	0.227	-2.99
$n\text{-}C_8H_{17}$	0.796	0.204	-3.32
$n\text{-}C_9H_{19}$	0.797	0.203	-3.34
C_6H_5	0.346^d	0.654	1.55
CH_2OH	0.365^e	0.635	1.35

Table II. Substituent Effects on the Selectivity of the Oxidation of $RCH=CH_2$ Alkenes by Thallium(III) Nitrate at 20°C

Substituent	Mol fraction		$\delta_R \Delta G^{\ddagger a}$
	Ketone	Diether	
CH_3	0.488	0.512	0.11
C_2H_5	0.395	0.605	1.05
$n\text{-}C_3H_7$	0.385	0.615	1.13
$n\text{-}C_4H_9$	0.396	0.604	1.05
$n\text{-}C_5H_{11}$	0.377	0.623	1.30
$i\text{-}C_3H_7$	0.345	0.655	1.55
$t\text{-}C_4H_9$	0.539	0.461	-0.49
$i\text{-}C_4H_9$	0.384	0.616	1.12
$n\text{-}C_8H_{17}$	0.280	0.520	1.55
C_6H_5	0.867^d	0.133	-4.56
CH_2OH	0.852^e	0.148	-4.27

[a] $\delta_R \Delta G^{\ddagger} = \Delta G_c^{\ddagger} - \Delta G_d^{\ddagger} = -2.303\ RT \log(X_c/X_d)$, kJ; [b] Data from ref.8; [c] Value from ref.9; [d] Phenylacetaldehyde; [e] Hydroxyacetone.

The slopes have relatively a lower absolute value which is in agreement with the assumption of the S_N2 mechanism of the formation of vicinal diol or diether[2]. The effect on the migration aptitude of H^- (H^- shift), giving ketone, is increased with electron-releasing substituents.

From Figure it is obvious that plots for oxidation in aqueous medium are practically inverse to the plot for oxidation in methanol and hence it follows that in consequence of the change of the solvent the reaction mechanism may be influenced. It is readily apparent that in aqueous solutions ketones are formed predominantly, while in methanol the formation of ketones is suppressed in favour of the formation of dimethoxyether. We propose two possible explanations for this fact. In the simplest terms, we would expect the activated complex for H^- shift to be stabilized by an increase in the dielectric constant of the solvent. Thus an increase in the dielectric constant should lead to an increase in rate of ketone formation. It is also possible to interpret the data in a way of increase in the relative nucleophilicity of methanol compared to water. In methanol solvent the S_N2 attack of oxythallation intermediate may be expected. In

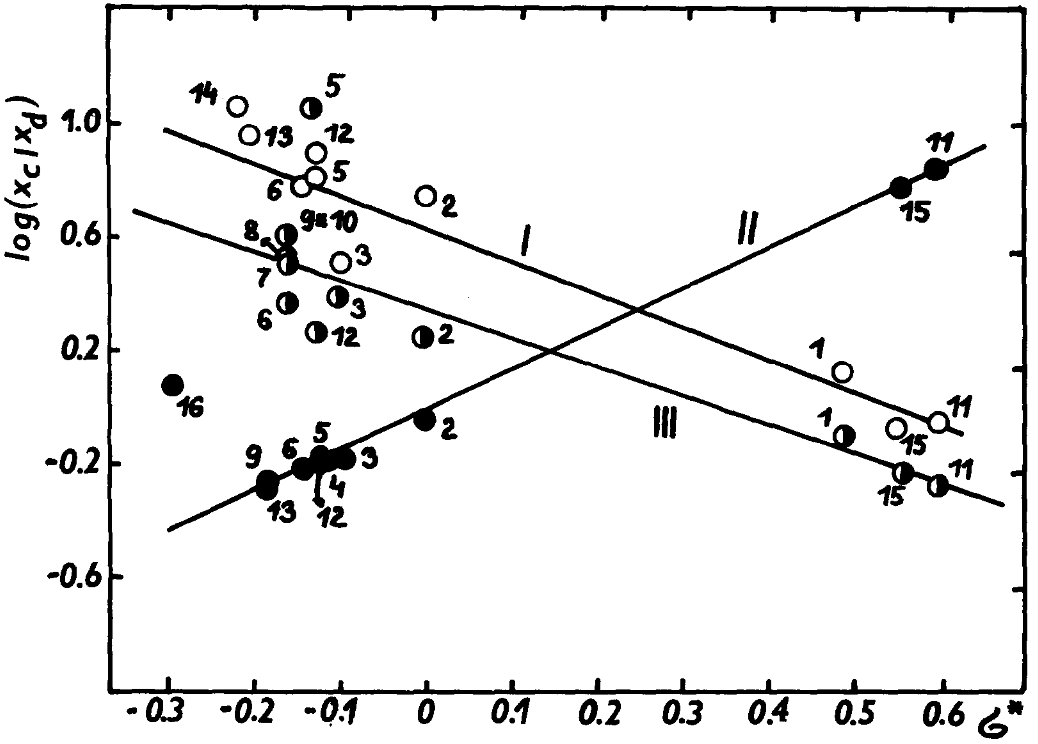


Figure: Medium and Substituent Effects on the Selectivity of the Oxidation of $RCH=CH_2$ Alkenes by Thallic Salts[11]. I, oxidation by $Tl_2(SO_4)_3$ in aqueous H_2SO_4[2], $(\rho_c^* - \rho_d^*) = -1.20$, $\log(k_c^o/k_d^o) = 0.62$, $r_{xy} = 0.950$, $S = 90.25\%$. II, oxidation by $Tl(NO_3)_3$ in methanol, $(\rho_c^* - \rho_d^*) = 1.40$, $\log(k_c^o/k_d^o) = -0.02$, $r_{xy} = 0.980$, $S = 96.05\%$. III, oxidation by $Tl(ClO_4)_3$ in aqueous $HClO_4$, $(\rho_c^* - \rho_d^*) = -0.82$, $\log(k_c^o/k_d^o) = 0.34$, $r_{xy} = 0.825$, $S = 68.06\%$.
1 ethylene, 2 propylene, 3 1-butene, 4 1-pentene, 5 1-hexene, 6 1-heptene, 7 1-octene, 8 1-nonene, 9 1-decene, 10 1-undecene, 11 styrene, 12 4-methyl-1-pentene, 13 3-methyl-1-butene, 14 1-dodecene, 15 allylalcohol, 16 3,3-dimethyl-1-butene

addition, S_N2 mechanism is facilitated with electron-withdrawing substituents on C=C bond. However, the phenyl group migration is much faster process than OCH_3 participation.

Thus we conclude that an aqueous medium is suitable for the preparation of the carbonyl compounds from alkenes with electron-releasing substituents; on the other hand, a methanol medium is more suitable for the formation of the carbonyl compounds from alkenes with electron-withdrawing substituents.

References and Notes

1. Part V in the series Extrathermodynamic Free Energy Relationships in the Oxidation of Alkenes by Thallic Salts; Part IV: M. Strašák, *Z. Naturforsch.* *33 b*, 224 (1978).
2. M. Strašák and M. Hrušovský, *J. Org. Chem.* *42*, 685 (1977).
3. M. Strašák and M. Hrušovský, *Collect. Czech. Chem. Commun.* *42*, 3278 (1977).
4. M. Strašák, *React. Kinet. Catal. Lett.* *7*, 387 (1977).
5. For a review see, M. Strašák, *Chem. Listy* *72*, 673 (1978).
6. See for example J.E. Leffler and E. Grunwald, "*Rates and Equilibria of Organic Reactions*", Wiley, New York, N.Y., 1963, p. 162.
7. All reactions were carried out at standard conditions: 150 ml of $Tl(ClO_4)_3$ in aqueous $HClO_4$ (0.38 M) or $Tl(NO_3)_3$ in methanol ($[Tl^{3+}]$ = 0.110 gion/l in both cases) and 10 ml (or 20 ml) of alkene was added (the molar ratio of alkene/Tl^{3+} was 4/1). The reaction mixture was stirred at 20°C until a starch-iodide test indicated complete reduction of Tl^{3+} to Tl^+. After the reaction was completed the aqueous and organic layers were separated and weighed. From the aqueous phase Tl^+ was precipitated in the form of insoluble TlCl by an equivalent amount of HCl. The latter product was transformed by boiling with 50% H_2SO_4 into Tl_2SO_4 (or with 50% $HClO_4$ into $TlClO_4$), which was returned to the electrochemical reoxidation. For the identification and quantitative determination of ketones and diethers the GC-MS method was employed. The diols obtained were determined by the periodate method[10].
8. P.M. Henry, *J. Amer. Chem. Soc.* *87*, 4423 (1965).
9. F. Goodridge and C.J.H. King, *J. Appl. Chem. Biotechnol.* *21*, 208 (1971).
10. G.O. Curme, "*Glycols*", Reinhold, New York, N.Y., 1952, p. 237.
11. The values of σ^* from R.W. Taft in "*Steric Effects in Organic Chemistry*", M.S. Newman, Ed., Wiley, New York, N.Y., 1956, Ch. 13.

(Received in UK 28 September 1978)