Substituent Effects in the Oxythallation of Alkenes*

Milan Strašák

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

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The rate constants for oxythallation of alkenes have been correlated with their experimental and calculated ionization potentials respectively. A good correlation between the rate constants and the ionization potentials of alkenes was found. It was found that inductive effects were the most important in the oxythallation of RCH—CH₂ and R²R²C—CH₂ alkenes.

From earlier studies [1, 2] it is obvious that the rate determining step of the oxidation of alkenes by thalllic salts is the formation of the intermediate oxythallation adduct according to Eq (1):

\[ R_2C = CR_2 + Tl^{3+} + H_2O \rightarrow [CR_2(OH)Cr_2Tl]^{3+} + H^+ \]  

(1)

where R = H and/or alkyl (aryl).

Presence of electron-releasing substituents on alkene double bond increases the rate of oxythallation - it is in accordance with Adg character of this reaction [2-5]. In earlier papers of this series we showed that oxidation of alkenes by an aqueous solution of thalllic salts suits Taft’s equation, and isokinetic relationship, too [6-8]. We studied the enthalpy – entropy relationship in this reaction and we found that the oxidation of alkenes by thalllic salts was the case, where both activation parameters were variable in the sense that their effects partially compensate each other [8, 9]. The determination of structure effects in oxidation was carried out using linear free energy relationship and it was found that polar effects were the most important for the oxidation of RCH=CH₂ and R²R²C=CH₂ alkenes while both steric and resonance effects were important in the oxidation of internal alkenes [6].

This paper concerns itself with the examination of the response of rate of oxythallation to changes in ionization potentials for a series of substituted alkenes.

* Part IV in the series: Extrathermodynamic Free Energy Relationships in the Oxidation of Alkenes by Thalllic Salts. Part III; see ref. [8].

Requests for reprints should be sent to M. Strašák, Department of Analytical Chemistry, Pharmaceutical Faculty, Komensky University, 880 34 Bratislava, Czechoslovakia.

Methods and Experimental

Ionization potentials

The experimental values of the photoionization potentials for various olefinic hydrocarbons were taken from the literature [10-12]. For calculation of the ionization potentials of alkenes, for which the experimental value is not yet available were used following LFER methods:

1. Method according to Levitt, Levitt and Párkányi [13] using \( \sigma_I \) constants [18]:

\[ I = I_{CH_4} + \varepsilon \sum \sigma_I \]  

(2)

2. Similar results can be obtain using \( \sigma^* \) constants [19]:

\[ I = I_{CH_6} + \varepsilon^* \sigma^* \]  

(3)


\[ I = I_{C_2H_4} + \varepsilon^* \mu^* \]  

(4)

where value of \( \mu^* \) can be calculated according to rule of decrease of inductive effect [15]:

\[ \mu^* = -0.1 (i_1 + i_2z + i_3z + ... + i_nz^{n-1}) \]  

(5)

where 0.1 - coefficient for comparison with Taft's \( \sigma^* \) constants; \( z \) - the decreasing factor, i.e., constant characteristic for weakening of inductive effect per one CH₂ group (in this case \( z = 0.5 \)); \( n \) - position index with respect to C=C bond; \( i_1, i_2, ..., i_n \) - number of carbon atoms at various positions with respect to reaction centre.

4. Finally, we used equation (6):

\[ I = \text{const} + \varepsilon^* \Sigma \sigma^* \]  

(6)

Using a linear regression analysis we found that

\[ I = 8.201 + 1.038 \Sigma \sigma^* \]  

(7)

Regression lines

The least squares method was used to calculate the regression lines and the corresponding correlation coefficients.

Kinetic measurements

The kinetics of oxythallation 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 due to the decrease of concentration of the \( \text{Tl}^{3+} \) ions. The kinetic measurements were carried out using concentrations appropriate to the spectral technique, i.e., with the concentration of \( \text{Tl}^{3+} \) ions 2.5 \( \times \) 10\(^{-5} \) to 2.0 \( \times \) 10\(^{-4} \) gion/1 and that of the alkene 2.5 \( \times \) 10\(^{-4} \) to 2.0 \( \times \) 10\(^{-3} \) mol/l. The concentration of sulfuric acid was 0.05 mol/l (\( \mu = 0.10 \text{M} \)) 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 (Palo Alto, California), while the rates of slower reactions were measured in a spectrophotometer VSU-2-P (Zeiss, Jena). The reaction temperature of 25 °C was kept at a chosen level within the limit of \( \pm 0.1 \) °C.

Results and Discussion

The kinetics of the oxythallation were followed in accordance with our earlier work [6]. These reactions exhibited second-order kinetics corresponding to the rate law defined by Eq (8):

\[
-\frac{d [\text{alkene}]}{dt} = -\frac{d [\text{Tl}^{3+}]}{dt} = k [\text{Tl}^{3+}] [\text{alkene}]
\]

The rate of reaction was determined by applying the stopped-flow method on a spectrophotometer Durrum-Gibson D-110 (Palo Alto, California), while the rates of slower reactions were measured in a spectrophotometer VSU-2-P (Zeiss, Jena). The reaction temperature of 25 °C was kept at a chosen level within the limit of \( \pm 0.1 \) °C.

Table I presents the experimental values of the rate constants of the second-order for the oxythallation of various olefinic hydrocarbons along with their corresponding experimental and calculated ionization potentials.

\[
-\frac{d \ln [\text{Tl}^{3+}]}{dt} = k [\text{alkene}] = k_{\text{obsd}}
\]

Table I. Values of the rate constants of the second order for oxythallation of alkenes by thallium(III) sulfate in aqueous sulfuric acid at 25 °C, and ionization potentials of alkenes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Alkene</th>
<th>( I_a ) eV (Exp.)</th>
<th>( I_a ) eV (Caled., Eq (2))</th>
<th>( I_b ) eV (Caled., Eq (3))</th>
<th>( I_c ) eV (Caled., Eq (4))</th>
<th>( I_d ) eV (Caled., Eq (7))</th>
<th>( k ) 1 ( \cdot ) mol(^{-1} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene</td>
<td>10.516</td>
<td>10.260</td>
<td>10.516</td>
<td>10.51</td>
<td>10.24</td>
<td>0.335</td>
</tr>
<tr>
<td>2</td>
<td>Propylene</td>
<td>9.73</td>
<td>9.73</td>
<td>9.71</td>
<td>9.74</td>
<td>9.73</td>
<td>9.423</td>
</tr>
<tr>
<td>3</td>
<td>1-Butene</td>
<td>9.61(^b)</td>
<td>9.58</td>
<td>9.54</td>
<td>9.58</td>
<td>9.62</td>
<td>18.80</td>
</tr>
<tr>
<td>4</td>
<td>1-Pentene</td>
<td>9.50</td>
<td>9.59</td>
<td>9.52</td>
<td>9.52</td>
<td>9.50</td>
<td>20.85</td>
</tr>
<tr>
<td>5</td>
<td>3-Methyl-1-butene</td>
<td>9.51</td>
<td>9.52</td>
<td>9.40</td>
<td>9.42</td>
<td>9.53</td>
<td>35.01</td>
</tr>
<tr>
<td>6</td>
<td>1-Hexene</td>
<td>9.54</td>
<td>9.55</td>
<td>9.46</td>
<td>9.46</td>
<td>9.56</td>
<td>25.72</td>
</tr>
<tr>
<td>9</td>
<td>1-Decene</td>
<td>9.51</td>
<td>9.55</td>
<td>9.46</td>
<td>9.42</td>
<td>9.56</td>
<td>2.51</td>
</tr>
<tr>
<td>10</td>
<td>Styrene</td>
<td>8.59(^b)</td>
<td>11.42</td>
<td>10.70</td>
<td>10.35</td>
<td>1.16</td>
<td>0.25</td>
</tr>
<tr>
<td>11</td>
<td>Allylalcohol</td>
<td>9.67(^c)</td>
<td>10.32</td>
<td>10.62</td>
<td>10.90</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>13</td>
<td>Methyl allyl ether</td>
<td>10.28</td>
<td>10.57</td>
<td>10.28</td>
<td>10.27</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>14</td>
<td>4-Chloro-1-butene</td>
<td>10.84</td>
<td>10.34</td>
<td>10.84</td>
<td>10.13</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>15</td>
<td>2-Methyl-2-pentene</td>
<td>8.56</td>
<td>9.54</td>
<td>9.58</td>
<td>9.58</td>
<td>8.61</td>
<td>49.60</td>
</tr>
<tr>
<td>16</td>
<td>trans-4-Methyl-2-pentene</td>
<td>8.99</td>
<td>9.40</td>
<td>9.42</td>
<td>9.02</td>
<td>81.90</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2,4,4-Trimethyl-2-pentene</td>
<td>8.34</td>
<td>9.21</td>
<td>9.26</td>
<td>8.40</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2-Methyl-1-pentene</td>
<td>9.06</td>
<td>9.52</td>
<td>9.50</td>
<td>9.00</td>
<td>27.80</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>2,4,4-Trimethyl-1-pentene</td>
<td>9.50</td>
<td>9.44</td>
<td>9.44</td>
<td>9.05</td>
<td>13.00</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2-Ethyl-1-hexene</td>
<td>8.93</td>
<td>9.33</td>
<td>9.30</td>
<td>9.30</td>
<td>8.94</td>
<td>22.03</td>
</tr>
<tr>
<td>21</td>
<td>a-Methylstyrene</td>
<td>10.89</td>
<td>10.70</td>
<td>10.89</td>
<td>9.84</td>
<td>1.79</td>
<td></td>
</tr>
</tbody>
</table>

\* Data from ref. [10], \(^a\) data from ref. [11], \(^c\) taken from ref. [12], \(^d\) values were calculated from the date in ref. [1].
Figures 1 and 2 show a plot of the rate constants of the second order for oxythallation of alkenes vs calculated and experimental ionization potentials respectively. If \( RCH=CH_2 \) and \( R^1R^2C=CH_2 \) alkenes are considered separately, we see reasonable correlations of \( \log k \) with \( I \) within each set (Fig. 1). (For simplification there is only straight-line \( \log k \) vs \( I\) (calcd., Eq 2) depicted. The other those are similar.)

The increase in reactivity along the series is parallel to that observed for similar reactions of alkenes with Pd and Hg\(^{2+}\) ions \([16]\). This suggests that the increase in reactivity should be attributed to the inductive effect. The electrophilic nature of the TiX\(_3\) makes the polar structure \( \text{Olefine}^+-\text{TiX}_2^- \) important in describing the transition state of the oxythallation reaction. One may expect, therefore, that the reactivity of an olefine toward TiX\(_3\) should increase with decreasing of ionization potential of substrate. Figures 1 and 2 illustrate this point for a series substituted ethylenes, and show that a linear relation exists between ionization potential and the \( \log k \) for TiX\(_3\) addition per \( \text{C=C} \) center.

Therefore, the reaction mechanism of formation of the oxythallation adduct involves two steps: a) the formation of a \( \pi \)-complex by an electrophilic attack of the Ti\(^{3+}\) ion on the double bond; b) the change of the \( \pi \)-complex into a \( \sigma \)-complex – this being the decisive step with respect to the reaction rate \([1, 17]\). The rate-determining step in this oxythallation reaction is believed to be formation of the intermediate which may be bridged carbonium ion:

\[
\begin{align*}
R_2C\equiv CR_2 & \xrightarrow{\text{TiX}_3} R_2C\equiv CR_2^- \\
\text{TiX}_3 & \rightarrow X^- \\
R_2C\equiv CR_2 & \xrightarrow{\text{H}_2\text{O}} R_2\text{C(OH)}\text{CR}_2\text{TiX}_2 \\
\text{TIX}_2 & \text{H}^+ \end{align*}
\]

A comparison of the experimental ionization potentials and those calculated using LFER methods shows that the agreement is the best for ionization potentials calculated according to Eqs (2) and (7). In the case of alkenes with electronegative or aryl substituents it may be expect the departures. When the substituent is hydrogen or alkyl group, transmission of inductive effect occur only on \( \sigma \)-bonds, while in the case of electronegative or aryl substituents, anomalies rise as a consequence of the resonance. These changes in ionization potentials must be related to the properties of the substituent groups. The electron donating property of the substituent group has been related to chemical reactivities of substituted ethylenes. These correlations indicate that the effect of alkyl substituents on the \( \pi \)-electron density is primarily an inductive or polar one. Qualitatively, these results show that electron accepting groups produce an increase in the ionization potential of ethylene while the addition of an electron donor group causes a decrease in ionization potential.

Table II. Regression analysis.

<table>
<thead>
<tr>
<th>Ionization potential</th>
<th>( RCH=CH_2 )</th>
<th>( R^1R^2C=CH_2 )</th>
<th>Internal alkenes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n ) ( r )</td>
<td>( S [%] )(^a)</td>
<td>( n ) ( r )</td>
</tr>
<tr>
<td>Calcd., Eq (2)</td>
<td>10 0.996     99.20</td>
<td>4 0.994     98.80</td>
<td>3 0.867     75.16</td>
</tr>
<tr>
<td>Calcd., Eq (3)</td>
<td>11 0.995     99.00</td>
<td>4 0.953     90.82</td>
<td>3 0.803     64.55</td>
</tr>
<tr>
<td>Calcd., Eq (4)</td>
<td>8 0.979     95.84</td>
<td>no correlation</td>
<td>3 0.758     57.53</td>
</tr>
<tr>
<td>Calcd., Eq (7)</td>
<td>11 0.816     66.59</td>
<td>4 0.950     90.33</td>
<td>3 0.864     74.66</td>
</tr>
<tr>
<td>Exp.</td>
<td>7 0.985     97.02</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) \( S = 100 r^2 \), the number of experimental results [\%] that can be brought objectively into context with the linear regression relation.
The results of regression analysis are shown in Table II. From Table II and Fig. 1 it is obvious that inductive effects are the most important in the oxythallation of $\text{RCH} = \text{CH}_2$ and $\text{R}^1\text{R}^2\text{C} = \text{CH}_2$ alkenes.