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CHEMISTRY CASSETTES

General Editor:
Peter Groves
The University of Aston in Birmingham


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ISBN O 85186 378 7

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Linear Free Energy Relationships

\[ \text{CH}_3\text{CH}_2\text{Br} > \text{MeCH}_2\text{CH}_2\text{Br} > \text{Me}_2\text{CHCH}_3\text{Br} >> \text{Me}_3\text{CCH}_2\text{Br} \]

nucleophilic displacement by \( \text{EtO}^- \)

\[ \begin{align*}
\text{OMe} & > \circ & \text{NO}_2 \\
\end{align*} \]
electrophilic "displacement" by \( \text{NO}_2^- \) (nitration)

1. RELATIVE REACTIVITY SERIES

\[ \begin{align*}
1 & \quad \text{RCO}_2\text{Me} + \text{NMe}_3 \underset{k}{\overset{\theta}{\rightarrow}} \text{RCO}_2^- + \theta \text{NMe}_4 \\
2 & \quad \text{RCO}_2\text{H} + \text{H}_2\text{O} \underset{k}{\overset{\theta}{\rightarrow}} \text{RCO}_2^- + \text{H}_2\text{O}^+ \\
\end{align*} \]

2. FIRST MAJOR STRUCTURE/REACTIVITY CORRELATION

3. STRAIGHT LINE PLOT: \(-\log K_{\text{RCO}_2\text{H}}\) vs. \(-\log K_{\text{RCO}_2\text{Me}}\)

ACKNOWLEDGEMENTS

The plots in schemes 3, 5, 7, 21, 25, 32 and 43 are reprinted, from the source listed under the scheme concerned, with the kind permission of the American Chemical Society, copyright holder of the last four. The plot in scheme 38 is reprinted with the kind permission of Professor J A Leisten and the Royal Society of Chemistry.
\[ \Delta G^0 = -2.303RT \log K \]
equilibrium constant

\[ \Delta G^\ddagger = -2.303RT \log [\frac{h}{kT}] \]
rate constant

4 RELATIONSHIP BETWEEN \( k \), \( \kappa \) AND \( \Delta G \)

5 PLOT OF DISSOCIATION OF \( RCO_2H \) v HYDROLYSIS OF \( RCO_2Et \)

6 STERIC EFFECTS IN \( RCO_2H \) DISSOCIATION v \( RCO_2Et \) HYDROLYSIS

7 ACID DISSOCIATION v ESTER HYDROLYSIS: \( m- \) AND \( p- \) SUBSTITUTED BENZOATES
Applying this general equation to the straight line in SCHEME 7:

$$\log k_X = \rho \log K_X + c$$  ...[1]

where $\rho$ is the slope of the line, $c$ the intercept, and $X$ is a designated $m$- or $p$-substituent in the benzene ring of the species concerned. It is also possible to write an exactly analogous equation restricted to the pair of unsubstituted compounds, i.e. where $X = H$:

$$\log k_H = \rho \log K_H + c$$  ...[2]

Then subtracting ...[2] from ...[1]:

$$\log k_X - \log k_H = \rho (\log K_X - \log K_H)$$  ...[3]

which may also be written in the form:

$$\log \frac{k_X}{k_H} = \rho \log \frac{K_X}{K_H}$$  ...[4]

**DERIVATION OF HAMMETT RELATION: 1**

By definition: $\log \frac{K_X}{K_H} = \sigma_X$ (substituent constant) ...[5]

i.e. $\log \frac{K_{p-NO_2}}{K_H} = \sigma_{p-NO_2}$, $\log \frac{K_{m-Me}}{K_H} = \sigma_{m-Me}$

...[4] from SCHEME 8 can thus be transformed into:

$$\log \frac{k_X}{k_H} = \rho \sigma_X$$  ...[6]

This is the most common representation of the Hammett relation.

**DERIVATION OF HAMMETT RELATION: 2**

<table>
<thead>
<tr>
<th>Substituent, X</th>
<th>$\sigma_{p-X}$</th>
<th>$\sigma_{m-X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me, C</td>
<td>-0.10</td>
<td>-0.20</td>
</tr>
<tr>
<td>Me</td>
<td>-0.07</td>
<td>-0.17</td>
</tr>
<tr>
<td>H</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MeO</td>
<td>+0.12</td>
<td>-0.27</td>
</tr>
<tr>
<td>HO</td>
<td>+0.12</td>
<td>-0.37</td>
</tr>
<tr>
<td>F</td>
<td>+0.34</td>
<td>+0.06</td>
</tr>
<tr>
<td>Cl</td>
<td>+0.37</td>
<td>+0.23</td>
</tr>
<tr>
<td>MeCO</td>
<td>+0.38</td>
<td>+0.50</td>
</tr>
<tr>
<td>Br</td>
<td>+0.39</td>
<td>+0.23</td>
</tr>
<tr>
<td>CN</td>
<td>+0.56</td>
<td>+0.66</td>
</tr>
<tr>
<td>NO_2</td>
<td>+0.71</td>
<td>+0.78</td>
</tr>
</tbody>
</table>

**SOME SUBSTITUENT CONSTANT, $\sigma_X$, VALUES**

**BASE-CATALYSED HYDROLYSIS OF 2-ARYLETHANOATES**

![Diagram showing base-catalysed hydrolysis of 2-arylethanoates](image)

\[ p = 0.82 \text{ (slope of straight line)} \]

**PLOT OF $\log \frac{k_X}{k_H}$ v. $\sigma_X$ FOR 2-ARYLETHANOATE HYDROLYSIS**
## Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{ArNH}_2 ) with ( 2,4-(\text{NO}_2)_2)C_6H_5Cl in EtOH (25°)</td>
<td>( k )</td>
<td>-3.19</td>
</tr>
<tr>
<td>2. ( \text{ArNH}_2 ) with ( \text{C}_6\text{H}_5\text{COCl} ) in ( \text{C}_6\text{H}_6 ) (25°)</td>
<td>( k )</td>
<td>-2.69</td>
</tr>
<tr>
<td>3. ( \text{ArCH}_2\text{Cl} ) solvolysis in aq. ( \text{Me}_2\text{CO} ) (69.8°)</td>
<td>( k )</td>
<td>-1.88</td>
</tr>
<tr>
<td>4. ( \text{ArO}^\ominus ) with EtI in EtOH (25°)</td>
<td>( k )</td>
<td>-0.99</td>
</tr>
<tr>
<td>5. ( \text{ArCO}_2\text{H} ) with MeOH (acid-catalysed, 25°)</td>
<td>( k )</td>
<td>-0.09</td>
</tr>
<tr>
<td>6. ( \text{ArCO}_2\text{Me} ) hydrolysis (acid) in aq. MeOH (25°)</td>
<td>( k )</td>
<td>+0.03</td>
</tr>
<tr>
<td>7. ( \text{ArCH}_2\text{CO}_2\text{H} ) dissociation in ( \text{H}_2\text{O} ) (25°)</td>
<td>( K )</td>
<td>+0.47</td>
</tr>
<tr>
<td>8. ( \text{ArCH}_2\text{Cl} ) with ( \text{I}^\ominus ) in ( \text{Me}_2\text{CO} ) (20°)</td>
<td>( k )</td>
<td>+0.79</td>
</tr>
<tr>
<td>9. ( \text{ArCH}_2\text{CO}_2\text{Et} ) hydrolysis (base) in aq. EtOH (30°)</td>
<td>( k )</td>
<td>+0.82</td>
</tr>
<tr>
<td>10. ( \text{ArCO}_2\text{H} ) dissociation in ( \text{H}_2\text{O} ) (25°)</td>
<td>( K )</td>
<td>+1.00</td>
</tr>
<tr>
<td>(standard)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. ( \text{ArOH} ) dissociation in ( \text{H}_2\text{O} ) (25°)</td>
<td>( K )</td>
<td>+2.01</td>
</tr>
<tr>
<td>12. ( \text{ArCN} ) with ( \text{H}_2\text{S} ) (base) in EtOH (60.6°)</td>
<td>( k )</td>
<td>+2.14</td>
</tr>
<tr>
<td>13. ( \text{ArCO}_2\text{Et} ) hydrolysis (base) in aq. EtOH (25°)</td>
<td>( k )</td>
<td>+2.51</td>
</tr>
<tr>
<td>14. ( \text{ArNH}_2^\ominus ) dissociation in ( \text{H}_2\text{O} ) (25°)</td>
<td>( K )</td>
<td>+2.73</td>
</tr>
</tbody>
</table>

## Calculation of Relative Reaction Rate

\[
\log \frac{k_{m-\text{NO}_2}}{k_H} = \rho \sigma_{m-\text{NO}_2}
\]

i.e.

\[
\log \frac{63.5}{1} = \rho \times 0.71 \quad \therefore \quad \rho = 2.54
\]

\[
\log \frac{k_{p-\text{MeO}}}{k_H} = \rho \sigma_{p-\text{MeO}}
\]

i.e.

\[
\log \frac{k_{p-\text{MeO}}}{k_H} = 2.54 \times -0.27 \quad \therefore \quad \frac{k_{p-\text{MeO}}}{k_H} = 0.21
\]

## Base-Catalysed Hydrolysis of \( \text{XC}_6\text{H}_5\text{CO}_2\text{Et} \)

\[
\text{CO}_2\text{Et} + \Theta \text{OH} \xrightarrow{k_x} \text{CO}_2\Theta + \text{EtOH}
\]

when \( X = m-\text{NO}_2 \):

\[
\rho_{m-\text{NO}_2} = 63.5
\]

when \( X = p-\text{MeO} \):

\[
\rho_{p-\text{MeO}} = ?
\]

## Effect of \( m \)-Substituents on Ester Hydrolysis

\[
\sigma_{m-\text{NO}_2} = +0.71
\]

\[
\frac{k_{m-\text{NO}_2}}{k_H} = 63.5
\]

\[
\sigma_{m-\text{Me}} = -0.07
\]

\[
\frac{k_{m-\text{Me}}}{k_H} = 0.66
\]
EFFECT OF m- v p-MeO ON ESTER HYDROLYSIS

BASE-CATALYSED HYDROLYSIS OF XCH₂₅CO₂Et: ρ = +2.51

Acid dissociation (H₂O)  ρ
XC₆H₅CO₂H          1.00 (standard reaction)
XC₆H₅CH₃CO₂H          0.49
XC₆H₅CH₂CH₂CO₂H          0.21
XC₆H₅CH=CHCO₂H          0.47

ρ VALUES FOR DISSOCIATION OF XCH₂₅CO₂H

1. XC₆H₅CO₂H + H₂O ⇌ XC₆H₅CO₂⁻ + H₃O⁺  
   p-N O₂

2. XC₆H₅CH₃OH + H₂O ⇌ XC₆H₅CH₃O⁻ + H₃O⁺  
   p-CN

after Taft, R W and Lewis, I C.,  
J Amer Chem Soc, 1958, 80, 2437

BENZOYLATION OF XC₆H₅NH₂: ρ = -2.69

COMPARISON OF AQUEOUS DISSOCIATIONS OF XC₆H₅CO₂H  
AND XC₆H₅OH
22. ELECTRONIC EFFECTS IN $p$-$NO_2C_6H_4CO_2H$ AND $p$-$NO_2C_6H_4OH$

DISSOCIATIONS

<table>
<thead>
<tr>
<th>Substituent, X</th>
<th>$\sigma^-_{p-X}$</th>
<th>$\sigma^+_{p-X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2Et$</td>
<td>0.68</td>
<td>0.45</td>
</tr>
<tr>
<td>COMe</td>
<td>0.84</td>
<td>0.50</td>
</tr>
<tr>
<td>CN</td>
<td>0.88</td>
<td>0.66</td>
</tr>
<tr>
<td>CHO</td>
<td>1.03</td>
<td>0.43</td>
</tr>
<tr>
<td>$NO_2$</td>
<td>1.27</td>
<td>0.78</td>
</tr>
</tbody>
</table>

23. $\sigma^-_X$ v. $\sigma^+_X$ FOR SOME ELECTRON-WITHDRAWING $p$-SUBSTITUENTS

24. SOLVOLYSIS OF $XC_6H_4CMe_2Cl$

25. $\log \frac{k_X}{k_H} v. \sigma_X$ FOR SOLVOLYSIS OF $XC_6H_4CMe_2Cl$

26. $S_{N1}$ SOLVOLYSIS OF $XC_6H_4CMe_2Cl$

27. THROUGH CONJUGATION WITH ELECTRON-DONATING $p$-SUBSTITUENTS
### Table: 

<table>
<thead>
<tr>
<th>Substituent, X</th>
<th>$\sigma^+_{p-X}$</th>
<th>$\sigma^-_{p-X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$</td>
<td>-0.18</td>
<td>-0.01</td>
</tr>
<tr>
<td>Me</td>
<td>-0.31</td>
<td>-0.17</td>
</tr>
<tr>
<td>MeO</td>
<td>-0.78</td>
<td>-0.27</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>-1.30</td>
<td>-0.66</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>-1.70</td>
<td>-0.83</td>
</tr>
</tbody>
</table>

**28.** $\sigma^+ \gamma \sigma^-$ FOR SOME ELECTRON-DONATING P-SUBSTITUENTS

$$\log \frac{k_x}{k_H} = \rho [\sigma_x + r (\sigma^+_{p-X} - \sigma^-_{p-X})]$$  \text{[7]}

**29.** YUKAWA-TSUNO RELATION

$$O\text{SiEt}_3 \rightarrow O\text{OH} \rightarrow X \quad + \quad \text{Et}_3\text{SiOH}$$

**30.** BASE-CATALYSED HYDROLYSIS OF XC$_6$H$_5$OSiEt$_3$.

**31.** TRANSITION STATES IN WHICH THROUGH CONJUGATION OPERATES

- $\rho = +3.52$
- $r = 0.50$
- $\rho = -4.54$
- $r = 1.00$ (by definition)

**32.** ACETOLYSIS OF 3-ARYL-2-BUTYL BROMYLATES

**33.** $S^\text{2}$ ACETOLYSIS OF 3-ARYL-2-BUTYL BROMYLATES

**34.** XC$_6$H$_5$ AS AN INTERNAL NUCLEOPHILE


[B$_5$ = p - BrC$_6$H$_4$SO$_2$]
**THREO 3-ARYL-2-BUTYL BROSYLATES**

**VARIATION IN YIELD OF THREO PRODUCT WITH SUBSTITUENT, X**

<table>
<thead>
<tr>
<th>Substituent, X</th>
<th>Yield of threo product - 2 *</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO</td>
<td>100%</td>
</tr>
<tr>
<td>p-Me</td>
<td>88%</td>
</tr>
<tr>
<td>m-Me</td>
<td>68%</td>
</tr>
<tr>
<td>H</td>
<td>59%</td>
</tr>
<tr>
<td>p-Cl</td>
<td>39%</td>
</tr>
<tr>
<td>m-Cl</td>
<td>12%</td>
</tr>
<tr>
<td>m-CF₃</td>
<td>6%</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>1%</td>
</tr>
</tbody>
</table>

* = % of reaction proceeding by internal attack

**DISTINGUISHABLE PRODUCTS FROM EXTERNAL AND INTERNAL NUCLEOPILIC ATTACK**

**HYDROLYSIS OF XCO₂H IN 99.9% H₂SO₄**
ACID-CATALYSED ESTER HYDROLYSIS - COMMON ($A_{Ac}2$) PATHWAY

POSSIBLE TAUTOMERIC EQUILIBRIUM IN PROTONATED METHYL ESTER

ACID-CATALYSED ESTER HYDROLYSIS - $A_{Ac}1$ PATHWAY

CYCLODEHYDRATION OF 2-PHENYLTRIARYLMETHANOLS
CYCLODEHYDRATION AS DEHYDRATION/INTERNAL ELECTROPHILIC SUBSTITUTION

Base-catalysed hydrolysis ($B_{AC}2$): $p = 2.51$

Acid-catalysed hydrolysis ($A_{AC}2$): $p = 0.03$

STABILISATION OF CARBONIUM ION INTERMEDIATE FROM ALCOHOL WITH X = Z = OMe
T.S. for base-catalysed hydrolysis (B\text{AC} 2)

T.S. for acid-catalysed hydrolysis (A\text{AC} 2)

TRANSITION STATES FOR B\text{AC} 2 AND A\text{AC} 2 ESTER HYDROLYSIS

\[
\log \frac{[R^*]}{[R_{-}]}_{\text{base}} - \log \frac{[R^*]}{[R_{-}]}_{\text{acid}} = \rho^*_0 \sigma^*_R \quad \ldots \ [8]
\]

EQUATION FOR OPERATION OF POLAR EFFECTS ONLY IN ESTER HYDROLYSIS

\[
\log \frac{[R^*]}{[R_{-}]} = \rho^*_0 \sigma^*_R \quad \ldots \ [9]
\]

GENERALISED TAFT POLAR EFFECT EQUATION

\[
\log \frac{[R^*]}{[R_{-}]} = \rho^*_0 \sigma^*_R + \delta E_s \quad \ldots \ [11]
\]

INCORPORATION OF VARIABLE STERIC PARAMETER, \( \delta E_s \)

ACID-CATALYSED HYDROLYSIS OF \( \sigma \)-SUBSTITUTED BENZAMIDES

\[
R \text{ in } \text{RCO}_2\text{Et} \quad \delta E_s
\]

\begin{align*}
\text{H} & \quad +1.24 \\
\text{Me} & \quad 0 \text{ (by definition)} \\
\text{Et} & \quad -0.07 \\
\text{ClCH}_2 & \quad -0.24 \\
\text{ICH}_2 & \quad -0.37 \\
\text{PhCH}_3 & \quad -0.38 \\
\text{Me(CH}_2)_3 & \quad -0.39 \\
\text{Me}_2\text{CHCH}_2 & \quad -1.13 \\
\text{Me}_3\text{C} & \quad -1.54 \\
\text{Me}_3\text{CCH}_2 & \quad -1.74 \\
\text{Ph}_2\text{CH} & \quad -1.76 \\
\text{Et}_3\text{C} & \quad -3.81
\end{align*}
Reaction

\[ \text{ArCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{ArCO}_2^- + \text{H}_3\text{O}^+ (\text{H}_2\text{O}) \]

\[ \text{by definition} \]

\[ \begin{align*}
&\text{H}_2\text{O} & 1.00 \\
&\text{aq. MeOH} (50\% \text{ H}_2\text{O}) & 1.60 \\
&\text{aq. EtOH} (70\% \text{ aq. dioxan}) & 1.83 \\
&\text{aq. EtOH} (85\% \text{ aq. EtOH}) & 2.54 \\
&\text{aq. Me}_2\text{CO} (20\% \text{ H}_2\text{O}) & -0.67 \\
&\text{MeOH} & -1.09 \\
&\text{EtOH} & -2.03 \\
&\text{Me}_2\text{CHOH} & -2.75 \\
&\text{Me}_3\text{COH} & -3.26 \\
\end{align*} \]

VARIATION OF \( \beta \) WITH SOLVENT

\[ \text{ArCO}_2\text{H} + \text{ROH} \rightleftharpoons \text{ArCO}_2^- + \text{ROH}^- \text{[R = H or Et]} \]

DISSOCIATION OF \( \text{ArCO}_2\text{H} \) IN HYDROXYLIC SOLVENTS

\[ \begin{align*}
\text{Me}_3\text{C-Cl} & \rightarrow \text{Me}_3\text{C}^+ & \text{Cl}^- & \rightarrow \text{Me}_3\text{C-S} \\
\text{slow} & \text{ion pair} & \text{intermediate} & \text{fast} \\
\text{[}S = \text{solvent}] \\
\end{align*} \]

\[ \log k_A - \log k_0 = \gamma_A - \gamma_0 \quad \ldots \quad [12] \]

GRUNWALD-WINSTEIN: STANDARD REACTION AND EQUATION

Solvent Parameter, \( \gamma_A \), Values

\[ \log \frac{k_A}{k_0} = m \gamma_A \quad \ldots \quad [13] \]

Grunwald-Winstein Equation

<table>
<thead>
<tr>
<th>Halide</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH(Me)Br</td>
<td>1.20</td>
</tr>
<tr>
<td>Me_3CCL</td>
<td>1.00 (by definition)</td>
</tr>
<tr>
<td>Me_3CBr</td>
<td>0.94</td>
</tr>
<tr>
<td>EtMe_2CBr</td>
<td>0.90</td>
</tr>
<tr>
<td>CH_3=CHCH(Me)Cl</td>
<td>0.89</td>
</tr>
<tr>
<td>EtBr</td>
<td>0.34</td>
</tr>
<tr>
<td>Me(CH_2)_3Br</td>
<td>0.33</td>
</tr>
</tbody>
</table>

SUBSTRATE PARAMETER, \( m \), VALUES
\[ A \rightarrow B \xrightarrow{k} A^\circ B^\circ \]
slow

**SLOW STEP REQUIREMENT FOR GRUNWALD-WINSTEIN**

**Equilibrium constant:**

\[ \Delta G^0 = -2.303RT \log k \]

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

**Rate constant:**

\[ \Delta G^+ = -2.303RT \log k \left( \frac{h}{kT} \right) \]

\[ \Delta G^+ = \Delta H^+ - T \Delta S^+ \]

\[ k' = \text{Boltzmann's constant} \]

\[ h = \text{Planck's constant} \]

**Relationship between \( \log k, \log k', \Delta G, \Delta H \text{ and } \Delta S \)**

1. \( \Delta H \) is linearly related to \( \Delta S \) for the series
2. \( \Delta H \) is constant for the series
3. \( \Delta S \) is constant for the series

**Conditions Necessary for Linear Free Energy Relationships**

**Further Reading**


