

Coulomb's Law: the equation

$$\text{Energy of electrostatic interaction} \propto \frac{q_1 q_2}{\epsilon r_{12}}$$

where  $q_1$  and  $q_2$  are the two charges (sign and magnitude)

$r_{12}$  is the distance between them

$\epsilon$  is the dielectric constant (a measure of "polarity", 1 for vacuum, 80 for water)

In words we can say the same thing as:

like charges repel

unlike charges attract

the farther apart the weaker the effect; the closer together, the stronger

polar solvents weaken the interaction; non polar solvents strengthen it.

A consequence of Coulomb's Law is the hierarchy of electrostatic interactions:

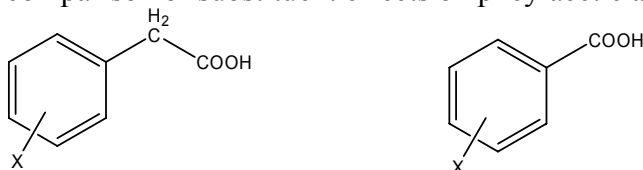
Charge-charge > charge-dipole > dipole-dipole > dipole-induced dipole > induced dipole-induced dipole.

## 5. Rate constant magnitudes. Linear free energy relationships

### (a) Introduction

A particularly powerful procedure for testing mechanistic hypotheses is to compare the rate constants of a series of reactions of the type under study with a corresponding standard series of rate or equilibrium constants. The series may be obtained by varying either (a) substituents in one of the reactants, (b) solvents, (c) acidic or basic catalysts, etc.

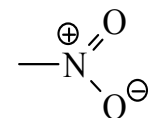
Now we will try to make more quantitative comparisons. First we will look at a comparison of substituent effects on phenylacetic acids vs benzoic acids,



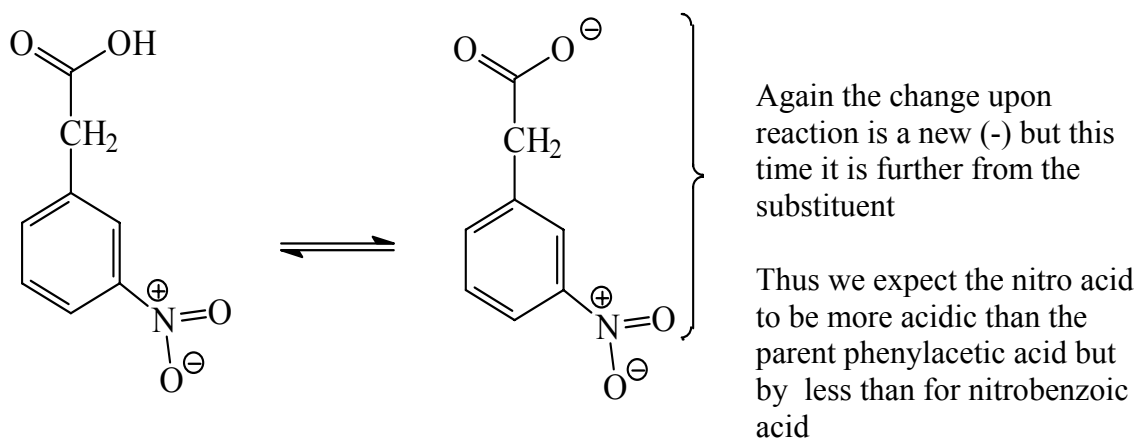
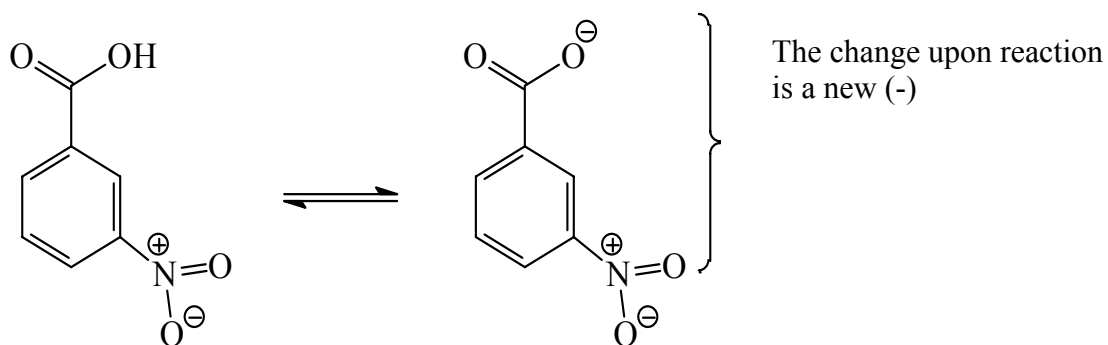
We do this by plotting  $\log K_a$  for the phenylacetic acids vs  $\log K_a$  for the benzoic acids

What do we expect from Coulomb's law?

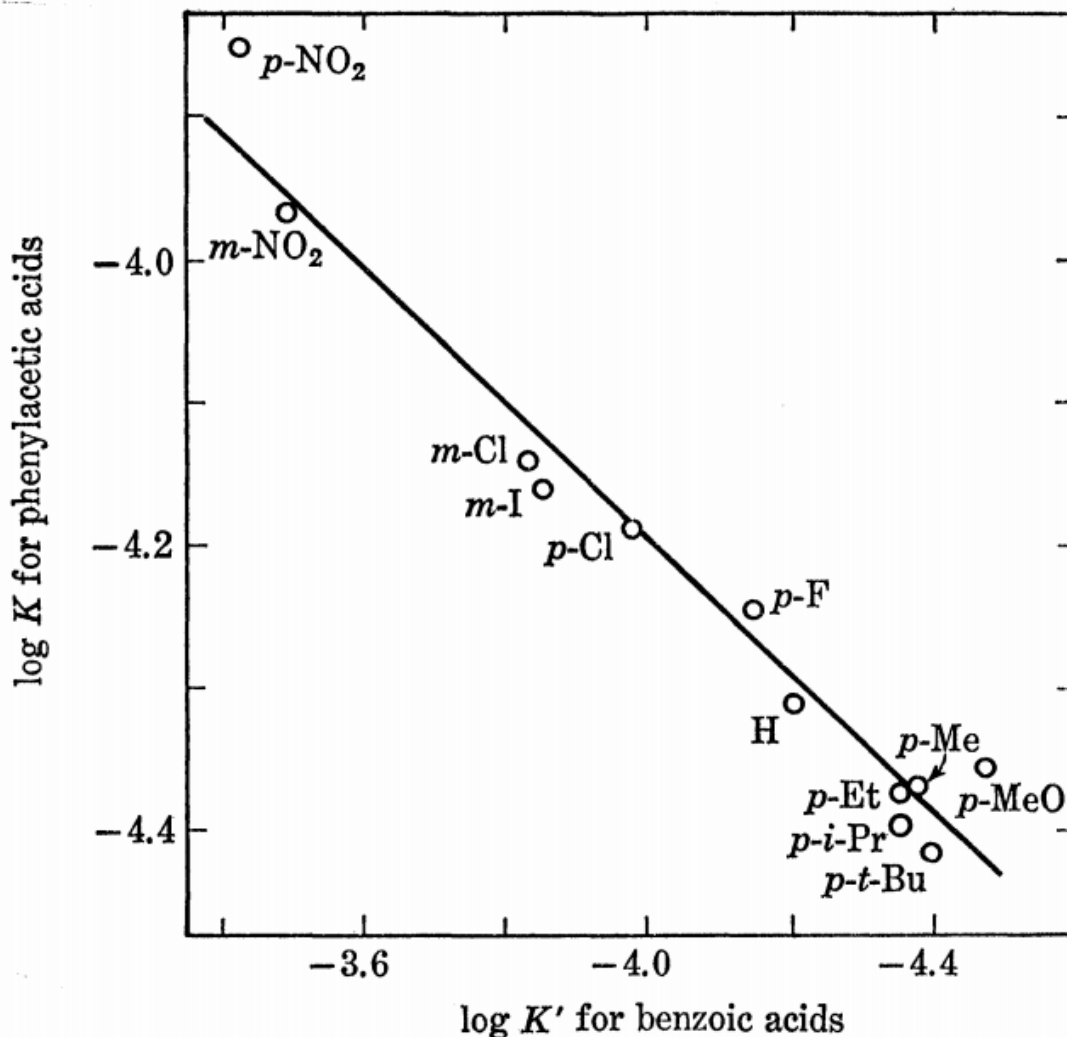
We will look at NO<sub>2</sub> as a good electron withdrawing group (EWG)



It has a dipole with the (+) end closer to the benzene ring; since electrostatic effects fall off with distance, the (+) is more important than the (-).

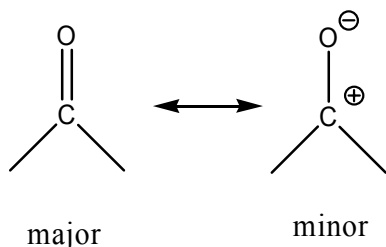


There will be a similar analysis for any substituted phenylacetic acid compared to a corresponding substituted benzoic acid. If we do this for a bunch of substituents we can get an average measure of sensitivity to the substituent. To do this we plot  $\log K_a(\text{ArCH}_2\text{COOH})$  vs.  $\log K_a(\text{ArCOOH})$ . The slope tells us the relative sensitivity; if they are equally sensitive to substituents the slope will be 1.0; if the substituted phenylacetic acids are less sensitive the slope will be less than 1.0. There will be some scatter because substituents do not act by pure coulombic effects.

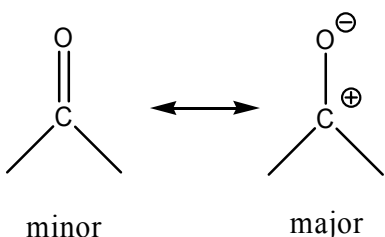


The slope of the graph is about 0.5, i.e. the effect of a substituent on the pK<sub>a</sub> of ArCH<sub>2</sub>COOH is about half the effect of the same substituent on ArCOOH. Such correlations are useful for predicting the pK<sub>a</sub> values for acids which have not been measured.

For this course using this approach to study the properties of transition states will be more important. Here we run into a problem. If we want to interpret reactions involving addition to a carbonyl or elimination to form a carbonyl we need to look at the nature of the carbonyl group. Years ago theoreticians suggested:



but more recently a lot of theoreticians are saying that really the situation is:



This is really another of the problems posed by quantum theory:  
 Is an electron a wave or a particle? Yes  
 Is a carbonyl a  $\pi$ -bond or a dipolar bond? Yes

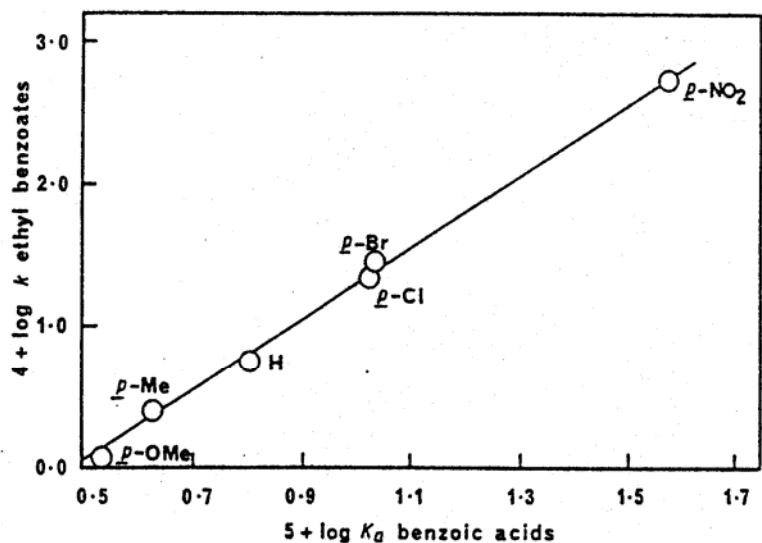
There is an additional problem when we look at rate constants; the sensitivity to substituents depends on whether the transition state is early or late. We often do not know as we start to study the reaction and we may not even know the equilibrium constant for the rate determining step.

What we do is look at the mechanism and ask, for the rate determining step:

- 1) what is the expected slope of the graph for  $\log K$  up to the start of the rate determining step.
- 2) what is the expected slope of the graph for  $\log K$  up to the end of the rate determining step.
- 3) The slope of the graph for  $\log k$  is expected to fall between these values and the observed value gives a rough measure of transition state position.

We will need to be able to estimate the slope of the graph of any  $\log K$  or  $\log K$  vs  $\log K_a(\text{ArCOOH})$ ; shortly we will present a method.

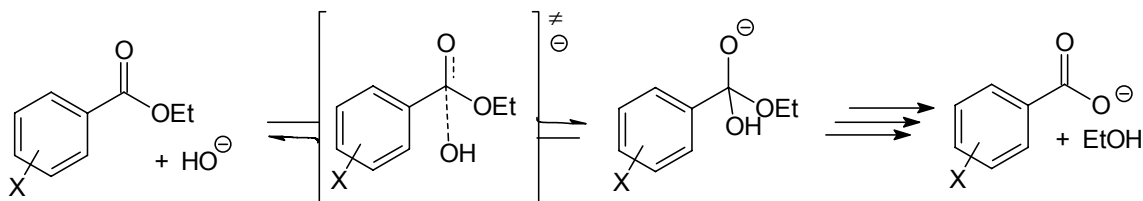
For example we compare the TS for hydroxide catalyzed hydrolysis of a series of benzoate esters with ionization of a series of benzoic acids. We are asking if there is a negative charge on the TS (as one would expect for addition of  $\text{HO}^-$ ). If there is a negative charge, then addition of a nitro group would stabilize it (EWG; positive end of the dipole for the nitro group is closer to the negative charge of the reaction center). How much? We use the ionization of benzoic acids as a reference; a p-nitro group makes benzoic acid more acidic by 0.78 in pKa.



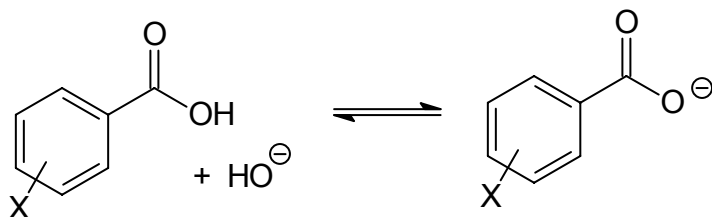
$k$  is the 2nd order rate constant for the reaction  
 $\text{ArCOOEt} + \text{OH}^- \rightarrow \text{ArCOO}^- + \text{EtOH}$   
 in 85% (w/w) EtOH:H<sub>2</sub>O at 25°C.

$K_a$  refers to  
 $\text{ArCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{ArCOO}^- + \text{H}_3\text{O}^+$   
 in H<sub>2</sub>O at 25°C.

The mechanism of ester hydrolysis is (the first step is rate determining):



and we compare it to the known reaction:



The slope of the plot of  $\log k$  vs  $\log K$  tells us how the rate of reaction responds to polar substituents. If the TS had no *new* charges developing, then the slope would be zero: substituents which changed the pK<sub>a</sub> of benzoic acid would have no effect on the rate because there was no change in interaction energy. If a negative charge develops then the slope is positive and the magnitude depends on the distance between the developing charge and the substituent (relative to the distance in benzoic acid). If a positive charge develops then the slope is negative (electron withdrawing substituents favor ionization of benzoic acid and disfavor development of a positive charge in the TS). In the present case hydroxide must add to the ester group so a negative charge develops, and electron withdrawing groups help, and the slope is positive.

Looking at the graph you see that the slope is somewhat over 2; part of the reason is that the test reaction is being run in 85% ethanol, while the reference reaction, ionization of benzoic acids, was measured in pure water. Coulombs law tells us that electrostatic interactions are larger in less polar solvents. A significant part is that the addition to the carbonyl is really cancelling a positive charge next to the ring, rather than creating a negative charge one bond away from the ring.

To see what we would expect for the effect of substituents on a reaction:  
(remember that we will compare to ionization of the corresponding substituted benzoic acids)

- 1) Ask what is the change in charge upon reaction?
- 2) Does the interaction of this charge with an EWG substituent make the reaction easier? the slope will be positive  
harder? the slope will be negative
- 3) How far apart are the substituent and the charge which changes in the reaction?  
the closer the larger the slope  
the farther the smaller the slope

Why is it called a Linear Free Energy Relationship (LFER)?

Recalling the equations seen earlier,

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln k = \ln\left(\frac{k_B T}{h}\right) - \frac{\Delta G^\ddagger}{RT}$$

a linear plot of  $\log k$  vs  $\log K$  (or  $\log k$  vs  $\log k$ , or  $\log K$  v  $\log K$ ) reflects a linear relationship between the set of  $\Delta G^\ddagger$ 's and the set of  $\Delta G^\circ$ 's (or between two sets of  $\Delta G^\ddagger$ 's or two sets of  $\Delta G^\circ$ 's). The linearity of such log-log plots therefore reveals a LINEAR FREE ENERGY RELATIONSHIP (LFER).

e.g.  $\log k = a \log K + c$                       where "a" and "c" are constants

Then

$$2.303 \log k = \ln k = a 2.303 \log K + 2.303 c = a \ln K + c'$$

$$\ln k = a \ln K + c'$$

translating to free energies

$$\begin{aligned} \ln\left(\frac{k_B T}{h}\right) - \frac{\Delta G^\ddagger}{RT} &= a\left(\frac{-\Delta G^\circ}{RT}\right) + c' \\ -\frac{\Delta G^\ddagger}{RT} &= a\left(\frac{-\Delta G^\circ}{RT}\right) + c' - \ln\left(\frac{k_B T}{h}\right) \\ \Delta G^\ddagger &= a\Delta G^\circ - RT\left(c' - \ln\left(\frac{k_B T}{h}\right)\right) \\ &= a\Delta G^\circ + c'' \end{aligned}$$

The fit to the straight line in the above plot is not perfect (though as these plots go it is pretty good). This is normal for LFER's - they show greater or smaller amounts of "noise". But it is still fair to say that for each substituent its effect on log K (and hence on  $\Delta G^\circ$ ) has a corresponding analogous (but not necessarily exactly analogous) effect on log k (and hence on  $\Delta G^\ddagger$ ). This is not really surprising in terms of the mechanism for the saponification of the ethyl benzoates as shown above.

Result:

A linear free energy relationship between the rates of saponification of ArCOOEt and the equilibrium constants for ionization of ArCOOH is not surprising. Perhaps what is more surprising is that LFER's of this type can be found in series involving very different structures, different charge types, very different solvents, etc. We now have a closer look at the LFER involving substituents on an aromatic system.

(b) The Hammett equation

The particular case of a series of reactions with different substituents at the meta and para positions of an aromatic reactant is treated by equations proposed by L.P. Hammett (1930's).

$$\text{for rates} \quad \log k_x/k_o = \rho\sigma_x$$

$$\text{or (generally better)} \quad \log k_x = \log k_o + \rho\sigma_x$$

where  $k_x$  is the rate constant for the compound with substituent x  
 $k_o$  is the rate constant for the compound with the reference standard substituent (H)

$\sigma_x$  is the substituent constant for X

$\rho$  is the reaction constant for this particular reaction

for equilibria

$$\log K_x / K_o = \rho\sigma_x$$

$$\text{or (generally better)} \quad \log K_x = \log K_o + \rho\sigma_x$$

where

$$\sigma_x = \log(K_a)_x - \log(K_a)_H$$

or

$$\sigma_x = (pK_a)_H - (pK_a)_x$$

where  $(K_a)_H$  and  $(pK_a)_H$  refer to benzoic acid, and  $(K_a)_x$  and  $(pK_a)_x$  to the x-substituted benzoic acid (in H<sub>2</sub>O at 25.0°C).

*E.g.* the  $pK_a$  of p-nitrobenzoic acid is 3.42

the  $pK_a$  of benzoic acid is 4.20 and so for the NO<sub>2</sub> group

$$\sigma_p = 4.20 - 3.42 = 0.78$$

In this way the table of  $\sigma$ -values shown on the next page was obtained.

Note that with each substituent there are different values for the meta and para positions.

**Table 7-11. Hammett Substituent Constants,  $\sigma$ , Based on the Ionization of Benzoic Acids<sup>b</sup>**

SUBSTITUENT	Meta-Position		Para-Position	
	$\sigma_{meta}$	ESTIMATED LIMIT OF UNCERTAINTY	$\sigma_{para}$	ESTIMATED LIMIT OF UNCERTAINTY
<b>CH<sub>3</sub></b>	<b>-0.069</b>	<b>0.02</b>	<b>-0.170</b>	<b>0.02</b>
CH <sub>2</sub> CH <sub>3</sub>		0.1	-0.151	0.02
CH(CH <sub>3</sub> ) <sub>2</sub>		-	-0.151	0.02
C(CH <sub>3</sub> ) <sub>3</sub>		0.03	-0.197	0.02
3,4-(CH <sub>2</sub> ) <sub>4</sub>	-		0.042	0.02
C <sub>6</sub> H <sub>5</sub>	0.06	0.05	-0.01	0.05
CF <sub>3</sub>	0.43	0.1	0.54	0.1
<b>CN</b>	<b>0.56</b>	<b>0.05</b>	<b>0.660</b>	<b>0.02</b>
<b>COCH<sub>3</sub></b>	<b>0.376</b>	<b>0.02</b>	<b>0.502</b>	<b>0.02</b>
CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.37	0.1	0.45	0.1
CO <sub>2</sub> H	(0.37)	0.1	(0.45)	0.1
CO <sub>2</sub> <sup>-</sup>	-0.1	0.1	0.0	0.1
CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	-0.16	>0.1	-0.21	>0.1
Si(CH <sub>3</sub> ) <sub>3</sub>	-0.04	0.1	-0.07	0.1
Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-		0.0	0.1
Ge(CH <sub>3</sub> ) <sub>3</sub>	-		0.0	0.1
Ge(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-		0.0	0.1
Sn(CH <sub>3</sub> ) <sub>3</sub>	-		0.0	0.1
Sn(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-		0.0	0.1
N <sub>2</sub> <sup>+c</sup>	1.76	0.2	1.91	0.2
NH <sub>2</sub> .	-0.16	0.1	-0.66	0.1
NHCH <sub>3</sub>			-0.84	0.1
N(CH <sub>3</sub> ) <sub>2</sub>	-		-0.83	0.1
NHCOCH <sub>3</sub>	0.21	0.1	0.00	0.1



$\text{N(CH}_3)_3^+$	0.88	>0.2	0.82	>0.2
<b><math>\text{NO}_2</math></b>	<b>0.710</b>	<b>0.02</b>	<b>0.779</b>	<b>0.02</b>
$\text{PO}_3\text{H}^-$	0.2	>0.1	0.26	>0.1
$\text{AsO}_3\text{H}^-$	-	-	-0.02	>0.1
$\text{OCH}_3$	0.115	0.02	-0.268	0.02
$\text{OC}_2\text{H}_5$	0.1	0.1	-0.24	0.1
$\text{O(CH}_2)_2\text{CH}_3$	0.1	0.1	-0.25	0.1
$\text{OCH(CH}_3)_2$	0.1	0.1	-0.45	0.1
$\text{O(CH}_2)_3\text{CH}_3$	0.1	0.1	-0.32	0.1
$\text{O(CH}_2)_2\text{CH}_3$	0.1	0.1	-0.34	0.1
<b><math>\text{OC}_6\text{H}_5</math></b>	<b>0.252</b>	<b>0.02</b>	<b>-0.320</b>	<b>0.02(?)</b>
<b><math>\text{OH}</math></b>	<b>0.121</b>	<b>0.02</b>	<b>-0.37</b>	<b>0.04</b>
$\text{OCOCH}_3$	0.39	0.1	0.31	0.1
$\text{SCH}_3$	0.15	0.1	0.00	0.1
$\text{SC}_2\text{H}_5$	-	-	0.03	0.1
$\text{SCH(CH}_3)_2$		-	0.07	0.1
$\text{SH}$	0.25	0.1	0.15	0.1
$\text{SCOCH}_3$	0.39	0.1	0.44	0.1
$\text{SCN}$		-	0.52	0.1
$\text{SOCH}_3$	0.52	0.1	0.49	0.1
$\text{SO}_2\text{CH}_3$	0.60	0.1	0.72	0.1
$\text{SO}_2\text{NH}_2$	0.46	0.1	0.57	0.1
$\text{S(CH}_3)_2^+$	1.00	>0.3	0.90	>0.3
$\text{SO}_3^-$	0.05	>0.1	0.09	>0.1
$\text{SeCH}_3$	0.1	0.1	0.0	0.1
<b><math>\text{F}</math></b>	<b>0.337</b>	<b>0.02</b>	<b>0.062</b>	<b>0.02</b>
<b><math>\text{Cl}</math></b>	<b>0.373</b>	<b>0.02</b>	<b>0.227</b>	<b>0.02</b>
<b><math>\text{Br}</math></b>	<b>0.391</b>	<b>0.02</b>	<b>0.232</b>	<b>0.02</b>
<b><math>\text{I}</math></b>	<b>0.352</b>	<b>0.02</b>	<b>0.18</b>	<b>0.1</b>
$\text{IO}_2$	0.70	0.1	0.76	0.1
$\text{CH=CHNO}_2^{\text{d}}$	0.34	0.03	0.26	0.03

From the compilation of D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

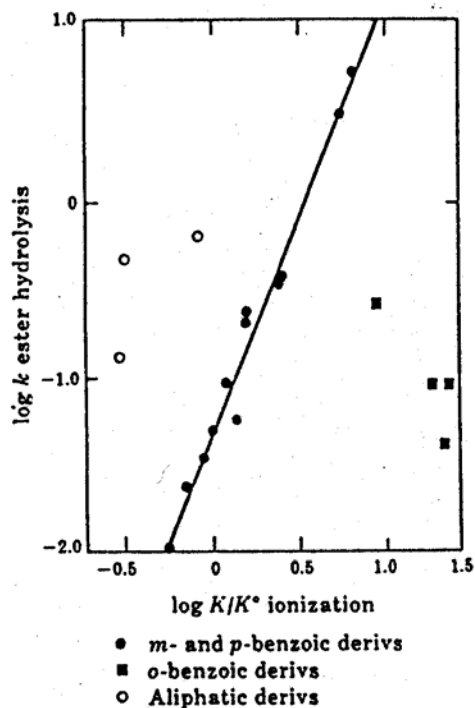
b Values in bold face are considered more reliable. It is recommended that reaction constants,  $\rho$ , be based on these values.

c. From E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, 81, 2070 (1959).

d From R. Stewart and L. G. Walker, *Can. J. Chem.*, 35, 1561 (1957).

#### Further points about Hammett plots

- (i) The series shown in the previous figure for rates of substituted ethyl benzoate hydrolysis was restricted to para-substituents. The following plot shows what happens when ortho and meta substituents and non-aromatic substrates are compared (The Hammett  $\rho\sigma$  treatment (in its simplest form) is restricted to meta and para substituents



Meta- and para-substituents give a good straight line. Ortho-substituents and the aliphatic compounds do not generally follow a simple Hammett relation. The deviations most commonly arise from steric factors, i.e. whereas steric effects are largely unchanged with change in meta- and para-substituents, ortho-substituents and aliphatic systems lead to different steric interactions with each case. With reactions of series of meta- and para-substituted aromatic compounds we are looking primarily at electronic effects - specifically, inductive (or field) and resonance effects.

- (ii) Electron-withdrawing substituents have positive  $\sigma$ -values; Electron-donating substituents have negative  $\sigma$ -values.

E.g.            *p*-NO<sub>2</sub>            0.78  
                   *m*-CN                0.56

vs

*p*-CH<sub>3</sub>            -0.17

- (iii) With two or more substituents (on the same or equivalent rings) the effects are often independent and additive, i.e.

$$\log k/k_0 = \rho \sum \sigma_x \quad \text{If they are not additive then something interesting is going on.}$$

or

- (iv) The sign and magnitude of the rho-value gives crucial information about the reaction.

If  $\rho$  is +ve

The reaction (like that of the standard reaction  $\text{ArCOOH} \rightarrow \text{ArCOO}^-$ ) is favoured by electron-withdrawing groups.

There is an increase in -ve charge close to the aromatic ring.

If  $\rho \sim 0$

The reaction is insensitive to the substituents;

There is no change in charge near the ring.

If  $\rho$  is -ve

The reaction is hindered by electron-withdrawing substituents.

There is an increase in the +ve charge close to the ring.

Two sets of examples:

(i) Equilibria -  $\log K$  vs  $\sigma$

Reaction	(conditions)	$\rho$
Ionization of $\text{ArPO}(\text{OH})_2$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	0.755
Ionization of $\text{ArPO}_2(\text{OH})^-$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	0.949
Ionization of $\text{ArOH}$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	2.11*
Ionization of $\text{ArNH}_3^+$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )**	2.77*
Ionization of $\text{ArNH}_3^+$	(20% dioxane: $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	3.26*
Ionization of $\text{ArNH}_3^+$	(82% dioxane: $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	3.43
Ionization of $\text{ArCH}_2\text{NH}_3^+$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	1.05
Ionization of substituted pyridinium ions	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	5.90
Ionization of $\text{ArCOOH}$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	1.0
Ionization of $\text{ArCH}_2\text{COOH}$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	0.67
Ionization of $\text{ArCH}_2\text{CH}_2\text{COOH}$	( $\text{H}_2\text{O}$ , $25^\circ\text{C}$ )	0.21

\* Some para-substituents consistently off this line ( $\text{NO}_2$ ,  $\text{COOR}$ ,  $\text{SO}_2\text{R}$  as is discussed later).

\*\* If written  $\text{ArNH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{ArNH}_3^+ + \text{H}_2\text{O}$ ,  $\rho = -2.77$ , etc.

(ii) Rates -  $\log k$  vs  $\sigma$

Reaction	(conditions)	$\rho$
$\text{ArCOOEt} + \text{HO}^-$	(85% $\text{EtOH}$ , $25^\circ\text{C}$ )	2.54
$\text{ArCOOEt} + \text{HO}^-$	(85% $\text{EtOH}$ , $50^\circ\text{C}$ )	2.32
$\text{ArCOOEt} + \text{HO}^-$	(60% acetone, $25^\circ\text{C}$ )	2.47
$\text{ArCH}_2\text{COOEt} + \text{HO}^-$	(60% acetone, $25^\circ\text{C}$ )	0.978.
$\text{ArCH}_2\text{COOEt} + \text{HO}^-$	$\text{EtOH}$ , $30^\circ\text{C}$ )	0.824

ArCH <sub>2</sub> CH <sub>2</sub> COOEt + HO <sup>-</sup>	(87.8% EtOH,30°C)	0.489
ArCH=CHCOOEt + HO <sup>-</sup>	(87.8% EtOH,30°C)	1.33
ArCONH <sub>2</sub> + HO <sup>-</sup>	(60% EtOH,52.8°C)	1.364
ArCONH <sub>2</sub> + H <sub>3</sub> O <sup>+</sup>	(60% EtOH,52.8°C)	-0.483
ArNMe <sub>2</sub> + CH <sub>3</sub> I	(90% acetone,35°C)	-3.30
ArCH <sub>2</sub> -CO-CH <sub>3</sub> + Br <sub>2</sub> + HClO <sub>4</sub>	(87%AcOH,25°C)	-0.22
ArCH <sub>2</sub> -CO-CH <sub>3</sub> + Br <sub>2</sub> + NaOAc	(87% AcOH,25°C)	1.73

Looking at the table of equilibrium  $\rho$  values we see that in the series ArOH, ArCOOH, ArCH<sub>2</sub>COOH, ArCH<sub>2</sub>CH<sub>2</sub>COOH the value of  $\rho$  progressively decreases. We can summarize this behavior in a very approximate rule: the rule of two. For each step closer to the benzene ring  $\rho$  gets a factor of two larger; for each step farther from the benzene ring  $\rho$  gets a factor of two smaller.

n	$\rho$
0	4
1	2
2	1.
3	0.5
4	0.25

There is also an important effect of solvent. The above values apply to equilibrium  $\rho$  values in water. We can look at the effect of changing to a less polar solvent:

Acid	solvent	$\rho$	ratio
ArCOOH	H <sub>2</sub> O	1.0	
ArCOOH	MeOH	1.54	1.5
ArCOOH	EtOH	1.957	2.0
ArCOOH	MeNO <sub>2</sub>	1.84	1.8
ArCOOH	PhCN	2.01	2.0
ArCOOH	MeCN	2.21	2.2
ArCOOH	propylene carbonate	2.00	2.0
ArCOOH	acetone	2.31	2.3
ArCOOH	formamide	1.31	1.3
ArCOOH	DMF	2.49	2.5
ArCOOH	DMSO	2.57	2.6
ArCOOH	MeOH	1.45	1.5
ArCOOH	EtOH	1.68	1.7
ArNH <sub>3</sub> <sup>+</sup>	H <sub>2</sub> O	2.77	2.8
ArNH <sub>3</sub> <sup>+</sup>	MeOH	3.01	1.1
ArNH <sub>3</sub> <sup>+</sup>	EtOH	3.54	1.3

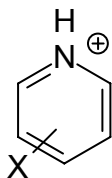
Summary: going from water to an organic solvent will increase the magnitude of  $\rho$  by a factor of about 2.0, except for a few solvents with small very polar molecules such as methanol or formamide.

Now let us work through the examples from the tables for equilibria.

Reactant		expect	find
ArPO(OH) <sub>2</sub>	log Ka	1	0.76

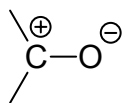
(but a C-P bond (1.8Å) is longer than a C-C bond (1.5Å) so we expect by Coulombs law that the effect on Ka will be smaller)

ArPO(O <sup>-</sup> )(OH)	log Ka	1	0.95
ArOH	log Ka	2	2.1
ArNH <sub>3</sub> <sup>+</sup>	log Ka	2	2.8
ArCH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	log Ka	1	1.05



	log Ka	4	5.9
ArCOOH	log Ka	1	1
ArCH <sub>2</sub> COOH	log Ka	0.5	0.67
ArCH <sub>2</sub> CH <sub>2</sub> COOH	log Ka	0.25	0.21

Approximate magnitudes of Hammett  $\rho$  values. A simple way to make approximate predictions of  $\rho$  values for carbonyl group reactions is to pretend that  $>C=O$



should be represented as:

Theoreticians have in fact argued that this charge separated resonance form is more important than is usually assumed by organic chemists. If we make this assumption, then protonation of the carbonyl oxygen in acetophenone, say, is in fact cancellation of a negative charge at the same distance from the benzene ring as the negative oxygen in benzoate ion, and thus the magnitude of  $\rho$  should be the same. It is in fact found to be 1.37