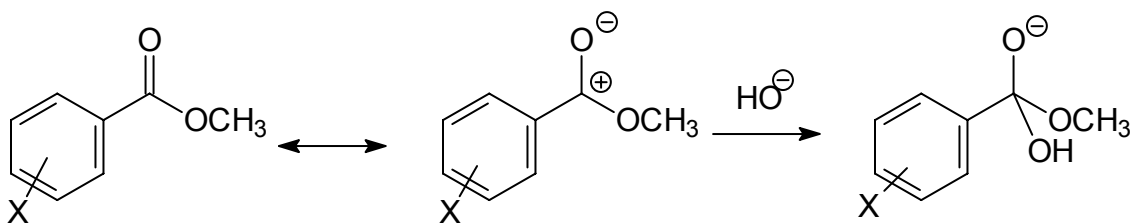
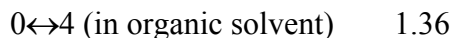


Addition of hydroxide to a benzoate ester leads to cancellation of the plus charge next to the ring, and thus the ρ is larger than for ionization of benzoic acid; in fact the equilibrium ρ is 2.04 in water.



Now let us work through the examples from the table for rates. Here we can only give a range from the ρ for an early TS (the equilibrium ρ up to the starting point for the rate determining step) to the ρ for a late TS (the equilibrium ρ up to the product of the rate determining step).

$\text{ArCOOEt} + \text{HO}^-$	$\log k$	$0 \leftrightarrow 2$ (in water) $0 \leftrightarrow 4$ (in organic solvent)	2.5
$\text{ArCH}_2\text{COOEt} + \text{HO}^-$	$\log k$	$0 \leftrightarrow 1$ (in water) $0 \leftrightarrow 2$ (in organic solvent)	0.98
$\text{ArCH}_2\text{CH}_2\text{COOEt} + \text{HO}^-$	$\log k$	$0 \leftrightarrow 0.5$ (in water) $0 \leftrightarrow 1$ (in organic solvent)	0.49
$\text{ArCH}=\text{CHCOOEt} + \text{HO}^-$	$\log k$	$0 \leftrightarrow 1$ (in water) $0 \leftrightarrow 2$ (in organic solvent)	1.33
(the double bond transmits polar effects better than CH_2CH_2 and in fact acts more like CH_2)			
$\text{ArCONH}_2 + \text{HO}^-$	$\log k$	$0 \leftrightarrow 2.0$ (in water)	1.07

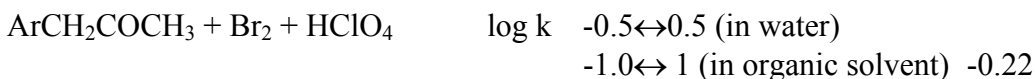


(This is a two step reaction: the first step is protonation on the carbonyl oxygen which cancels a minus charge at the same distance as the minus charge in benzoate, so $\rho = -1.0$ in water. The second step is addition of water which cancels the plus charge on nitrogen (in $\text{Ar-C}^+(\text{OH})\text{-NH}_2$) which is one step closer to the benzene ring than the minus in benzoate, for a contribution of $+2.0$ in water, and adds a new plus charge at the distance of the new OH_2^+ for a contribution of -1 . (The proton is likely to move off to a solvent water molecule, but this is unlikely to happen at the transition state because the pK_a of the OH_2^+ in the tetrahedral intermediate is only a bit more negative than that of water, and thus the proton transfer does not become favorable till far along the reaction coordinate, after the transition state.) We expect the second step to be rate determining and not the first. The net ρ from starting material to the adduct is $-1 + 2 - 1 = 0$, in water or -1.3 to -2.0 in an organic solvent. Moving the proton from oxygen to nitrogen to give a good leaving group for acid formation leads to no change in cumulative ρ . Losing the NH_3 causes formation of a $(+)$ charge on $\text{ArC}^+(\text{OH})_2$ one step closer to the benzene ring than the $(-)$ in benzoate for a contribution of -2 and loss of the charge on NH_3^+ at the same distance as the $(-)$ in benzoate for a contribution of $+1$; the net cumulative ρ to the protonated acid is $0 - 2 + 1 = -1$ (the same as for protonated amide)

stage	ArCONH_2	$\text{ArC(OH)(NH}_2)^+$	$\text{ArC(OH)(OH}_2)(\text{NH}_2)^+$	$\text{ArC(OH)}_2(\text{NH}_3)^+$	ArC(OH)_2^+
water	0.0	-1	0.0	0.0	-1
org.solv.	0	-2	0	0	-2
observed			-0.48		(or -0.48)

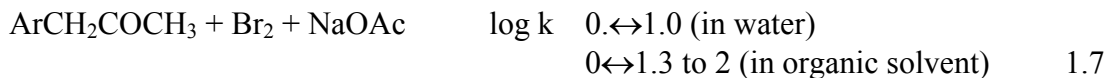


Here the new $(+)$ charge develops one step closer to the benzene ring than the $(-)$ in benzoate



(The rate determining step is enolization of the protonated ketone. Protonation of the ketone (cancelling a minus charge one step farther from the benzene ring than the minus in benzoate) leads to a ρ of -0.5 in water, which would become -1.0 in an organic solvent. Complete formation of the enol would involve cancellation of both the minus charge (contribution of -0.5) and of the plus charge of the carbonyl (here the plus charge is at the same distance as the minus of benzoate for a contribution of $+1.0$) with a net ρ value of $+0.5$ in water or $+1$ in organic solvent.)

stage	$\text{ArCH}_2\text{C}^+(\text{O}^-)\text{CH}_3$	$\text{ArCH}_2\text{C}^+(\text{OH})\text{CH}_3$	$\text{ArCH}=\text{C}(\text{OH})\text{CH}_3$
water	0.0	-0.5	+0.5
org.solv.	0.0	-1.0	+1.0
observed			-0.22



The rate determining step is enolate formation. This cancels the plus charge on carbon (the C=C of the enolate is best regarded as a true double bond) at the same distance from the benzene ring as the minus charge in benzoate for a ρ for a very late TS of 1.0 in water or 1.3 to 2. in organic solvent.

Review and Summary:

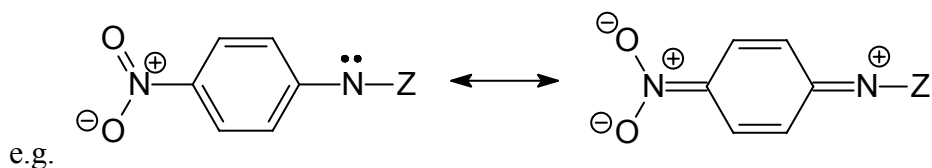
For kinetics, ρ is a way of asking about change in charge between SM and TS. We estimate ρ up to the start of the rds and at the end of the rds. Hammond's postulate implies that a late transition state means an "uphill" reaction, an early transition state means a "downhill" reaction, and a central transition state means no large change in energy from SM to Product.

Hammett equation - systematic deviations are found in some circumstances

Note

The deviant points are all due to para-substituents.

The deviant para-substituents are $-\text{NO}_2$, $-\text{CO-Z}$, $-\text{CN}$, $-\text{SO}_2\text{R}$, all groups capable of π -delocalization:



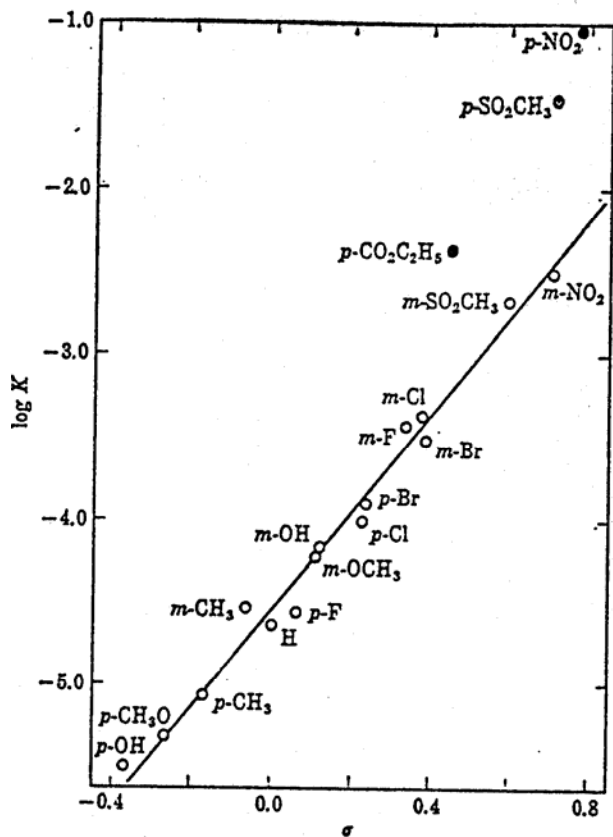


FIG. 4-2. Log K for acidity constants of anilinium ions vs. σ .

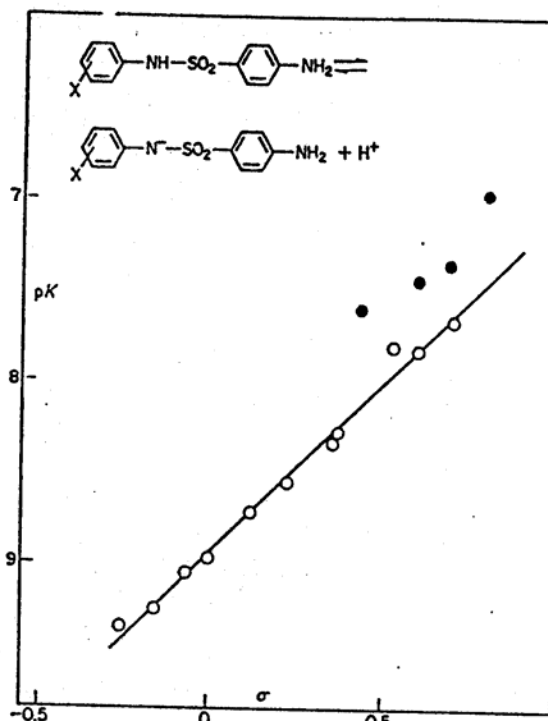
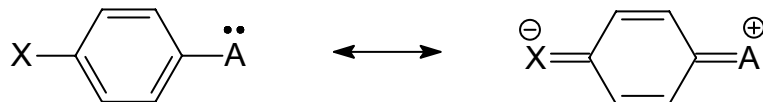


FIG. 1.2. A Hammett plot with deviating $-M$ *para*-substituents due to an electron-rich conjugated reaction centre; ionisation of N^1 -arylsulphanilamides²¹³ (● $-M$ *para*-substituents.)

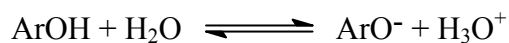
FIG. 4.2. A Hammett plot with deviating EWG *para*-substituents because of an electron-rich conjugated reaction centre; ionisation of anilinium ions (● EWG *para*-substituents.)

FIG. 1.2. A Hammett plot with deviating EWG *para*-substituents because of an electron-rich conjugated reaction centre; ionisation of N^1 -arylsulphanilamides (● EWG *para*-substituents.)

Similar deviations are always observed in reactions in which one of the components is stabilized by delocalization (and the other cannot be, or is much less so).



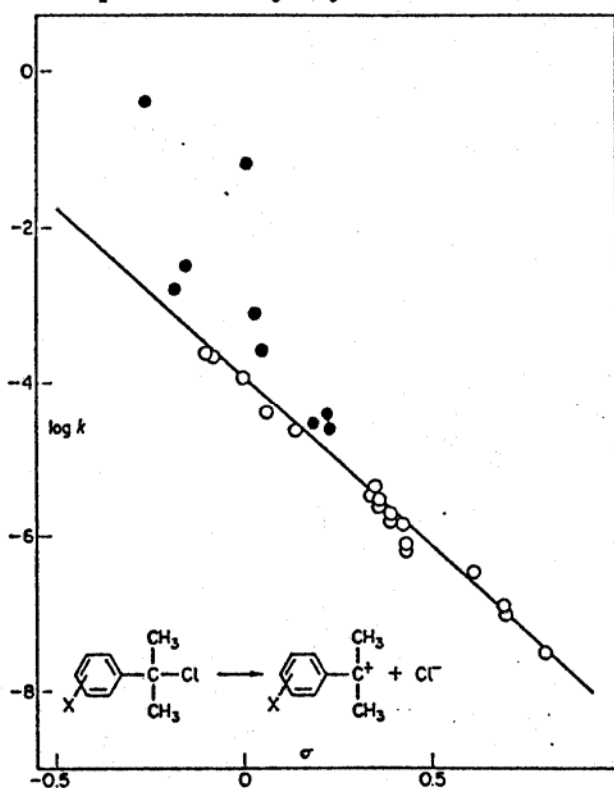
E. g.



(ArO^- stabilized by the π -delocalization, much more than ArOH)

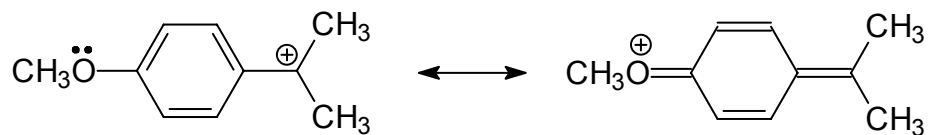
One approach is to define a new set of values, called σ^- , to be used whenever such a situation comes into play. The situation is a conjugative delocalization not possible in benzoic and therefore not accounted for in the ordinary σ value.

(ii) Before we finish our discussion of σ^- we note the complementary systematic deviation.



A Hammett plot with deviating EDG para-substituents because of an electron-deficient conjugated reaction centre; solvolysis of substituted t-cumyl chlorides. (● EDG para-substituents).

In this case it is evident that the most strongly deviant substituents are all para-substituents of the type \bar{A} -, e.g. NH_2 -, MeO -, HO - etc. Stabilization of the cation as follows



is to be expected. Similar, though slightly smaller, stabilization is presumably present in the transition state leading to the cation.

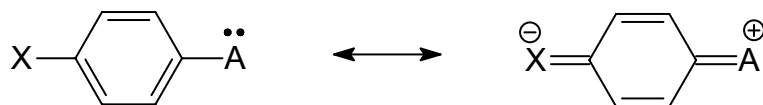
For these reactions a new set of substituent constants, called σ^+ values, may be used.

TABLE . Hammett Substituent Constants¹

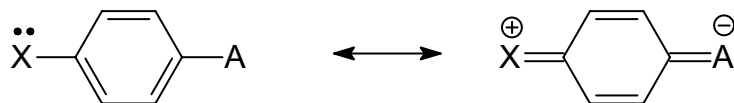
Substituent	σ_{para}	σ_{meta}	σ_{p}^+	σ_{p}^-
NH ₂	-0.66	-0.16	-1.3	
OH	-0.37	0.12	-0.92	
OCH ₃	-0.27	0.12	-0.78	-0.2
CH ₃	-0.17	-0.07	-0.31	-
NHCOCH ₃	-0.01	0.21	-0.25	
C ₆ H ₅	-0.01	0.06	-0.17	-
F	0.06	0.34	-0.07	-0.02
I	0.18	0.35	0.13	-
Cl	0.23	0.37	0.11	-
Br	0.23	0.39	0.15	-
OCOCH ₃	0.31	0.39	0.18	-
CO ₂ H	0.45	0.37	0.42	-
CO ₂ CH ₃	0.45	0.37	0.48	0.68
COCH ₃	0.50	0.38	-	0.87
CF ₃	0.54	0.43	0.58	-
CN	0.66	0.56	0.66	0.90
NO ₂	0.78	0.71	0.79	1.24
N(CH ₃) ₃ ⁺	0.82	0.88	0.64	-

¹Values are collected from C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 2, 323 (1964) and C. Hansch, A. Leo, S. Unger, K. H. Kim, D. Nakaitani, and E. J. Licm, *J. Med Chem.*, 16, 1207 (1973).

At this stage one might well ask the question which substituent constant should I use, σ , σ^+ , σ^- , or what? If one is studying a reaction in order to determine its mechanism, the answer is simple. Use the one that gives the best fit! If, for example, the fit with σ^- is clearly better than that for σ , this is evidence for a mechanism involving delocalization of the type



On the other hand if the fit with the σ^+ is best then this is most consistent with delocalization of the type

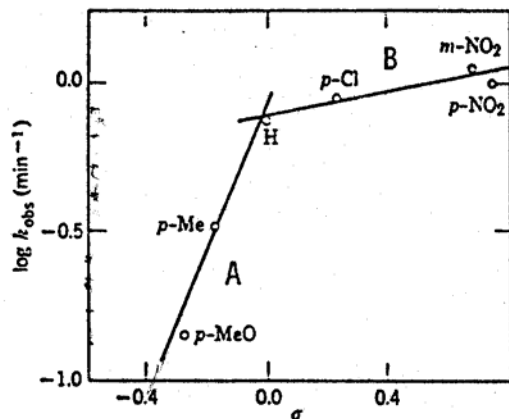


(Note: In these examples X is a substituent, A the "reacting part" of the molecule).

Finally, if the fit is best with σ , then neither of the above π -delocalization pictures is likely.

Hammett equation - non-linear correlations

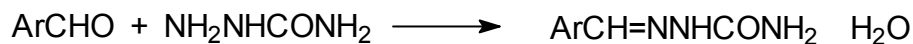
Failure to obtain a good linear correlation need not be a disaster - quite the contrary.



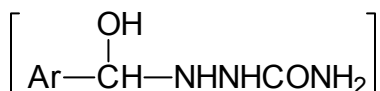
Concave down - change in RDS (The reaction occurs at the SLOWER of the two possible reactions, therefore they must be sequential so that the slower is the RDS. Better phrasing: the higher of the two transition state energy barriers controls the observed rate of reaction.)

The formation of semicarbazones from substituted benzaldehydes at pH 3.9.

Reaction

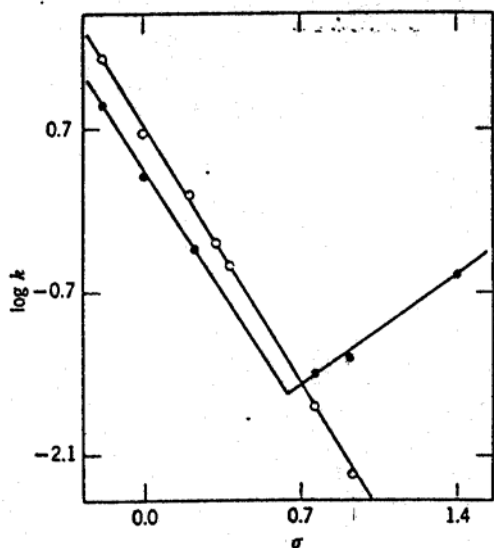


at pH 3.9 at 25°C



The Hammett plot consists of two straight lines. The break arises because of a change in rate determining step (in agreement with other experiments). With the substituents correlated by line (A) the first step is rate determining. ($k_{obs} = k_1$) At the break point step 1 and step 2 are of comparable rate and with higher σ -values the first step is no longer rate determining; $k_{obs} = K_1k_2$ and a different (smaller) slope is observed.

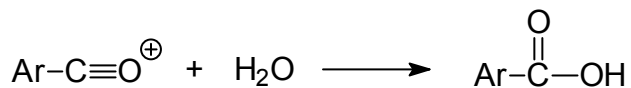
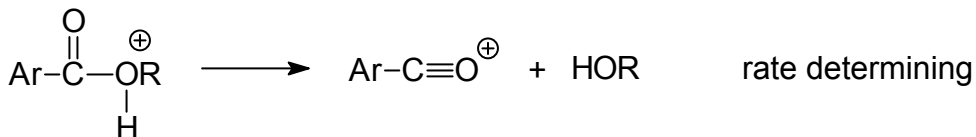
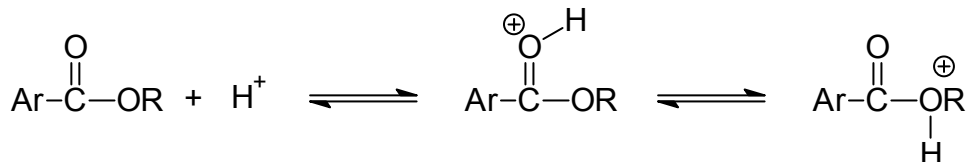
Another example.



Concave upwards - incursion of a new reaction. The reaction occurs at the faster of the two alternatives, therefore it is a simple competition between two paths and occurs by the faster of the two.

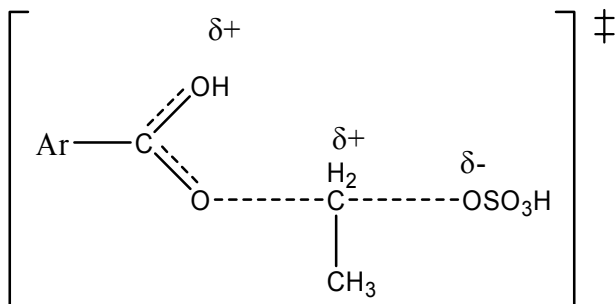
Hydrolysis of benzoate esters in 99.9% sulphuric acid. The open circles are for methyl esters, the filled circles for ethyl esters; k is in units of hr^{-1} .

The methyl esters and some of the ethyl esters (those with the more electron-donating substituents) are believed to react by the following path:



(the last step happens during workup)

With the ethyl esters there is an abrupt change in slope of the Hammett plot. This has been suggested to arise from incursion of the following process:



This is an SN2 substitution (a primary Et⁺ cation is too high energy to be involved); the transition state has extensive C-O bond breaking (good leaving group) and only a small amount of bond making (poor nucleophile). Such an “exploded” transition state would account for the Hammett plot as well. For this kind of transition state, with a lot of (+) character on the reaction center, ethyl would be faster than methyl.

The Hammett equation - improvements and extensions.

If the relative contributions of inductive and resonance effects were always the same as with the ionization of benzoic acids there would be no need for σ^+ or σ^- . The general difficulty is that the relative contributions of "through resonance" is specific for each reaction; i.e. neither σ , σ^+ nor σ^- may yield a good correlation with a particular series of reaction rates. One approach is to use an adjustable parameter related to the extent of the resonance interactions.

$$\log k/k_0 = \rho(\sigma + r[\sigma^+ - \sigma]) \text{ Yukawa-Tsuno equation}$$

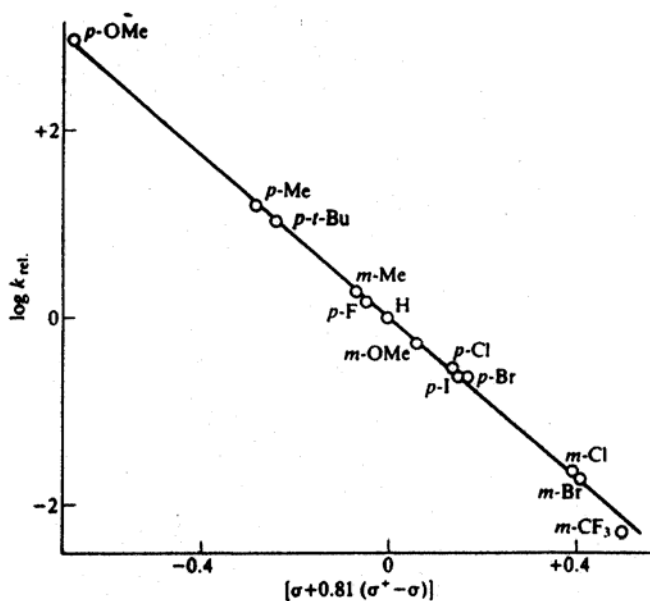
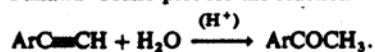
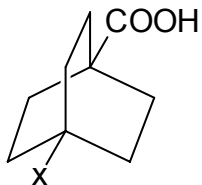


Fig. 4.9 Yukawa-Tsuno plot for the reaction⁷⁷



As an illustration of an extension of the Hammett equation, we note that set of σ values which should reflect only polar effects have been defined for the following system:



These values are called σ_x' and the relationship becomes:

$$\text{Log } K_x/K_0 = \rho' \sigma_x'$$

$$\text{or } \log K_x = \log K_0 + \rho' \sigma_x'$$

Taft equation

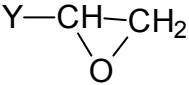
Taft has extended the Hammett relation to aliphatic species generally, leading to ρ^* , σ^* , and E_s (a steric parameter)

Taft substituent constants

X	$\sigma^*(X)$	$\sigma^*(CH_2X)$	X	$\sigma^*(X)$	$\sigma^*(CH_2X)$
Me	0.00	-0.10	OH	1.34	+0.555
Et	-0.10	-0.10	OMe	1.81	+0.52
n-Pr	-0.10	-0.13	OPh	2.43	+0.85
n-Bu	-0.13	-0.23	OEt	1.86	
isoPr	-0.19	-0.19	F	3.21	+ 1.1
isoBu	-0.125		Cl	2.96	+1.05
t-Bu	-0.300	-0.165	Br	2.84	+1.00
neoPe	-0.165		I	2.46	+0.85
Ph	+0.60	+0.215	NO ₂	4.25	+1.40
PhCH ₂	+0.215	+0.08	CN	3.60	+1.30
PhCH ₂ CH ₂	+0.08		CF ₃	2.61	+0.92
H	+0.49	0.00	CH ₃ CO	1.81	+0.60

Taft Reaction Constants

Reaction	ρ^*	log K	solvent
Equilibria		log K	
Ionization of acids, Y-COOH	+1.62	-4.66	water
Ionization of acids, Y-CH ₂ COOH	+0.67	-4.76	water
Ionization of alcohols, Y-CH ₂ OH	+1.32	-15.74	water
Ionization of ammonium ions, YY'Y''NH ⁺	+3.30	-9.61	water
Ionization of ammonium ions, (YCH ₂)(Y'CH ₂)(Y''CH ₂)NH ⁺	+1.83	-10.7	water

Rates		$\log(k_{Me}/s^{-1})$	
Alkaline hydrolysis of esters, Y-COOEt	+2.48		
Hydrolysis of acetals, Y-CH(OEt) ₂	-3.65	-0.73	50% aq dioxane
Esterification, Y-CH ₂ COOH + Ph ₂ CN ₂	+1.18	-1.94	ethanol
Bromination of PhCOCHYY' (Br ₂ , H ₂ O)	+1.59	-4.63	water
Bromination of YY'C=CYY''Y''' (Br ₂ , MeOH, NaBr)	-3.10		methanol
Acidic hydrolysis of		-1.83	-2.52
			aq HClO ₄
Acetolysis of YY'CHOBros	-3.49		HOAc
Ethanolysis of YY'Y''C-Cl	-3.29		80% aq EtOH
Ethanolysis of YCH ₂ OTos	-0.74		EtOH
RCH ₂ Br + PhS-	-606		MeOH

The rule of two can also be used to estimate ρ^* values for aliphatic systems. The major difference is that where ρ for substituted benzoic acids was 1.0, ρ^* for substituted formic acids is 1.6.

Number of atoms separating R from the reaction center	ρ^*
0	3.2
1	1.6
2	0.8
3	0.4

Alternatively, Taft and Swain respectively, have devised schemes for separating resonance and inductive effects. The former leads to σ_I and σ_R values, the latter to \mathcal{F} and \mathcal{R} (or F and R values). (The most recent paper by Swain, et al on this topic: *J. Am. Chem. Soc.* 105, 492 (1983)).

Taft's full proposal: $\log(k_X/k) = \rho_I \sigma_I + \rho_R \sigma_R + E_S$
This is intended to be a very general formulation.

Since k_A (acid catalyzed ester hydrolysis) showed very little dependence on σ 's, this could yield

$$\log \frac{(k_A)_X}{(k_A)_H} \approx E_S$$

For aliphatic systems, $\log(k_X/k) = \rho_I \sigma_I + E_S$

For the σ_m and σ_p correlations we may assume that E_S is small, and so for simple aromatic systems

$$\log(k_X/k) = \rho_I \sigma_I + \rho_R \sigma_R$$

With due diligence we may find σ_I and σ_R values.

Empirically

$$(\sigma_I)_X = 0.45 \sigma_{CH_2X}^*$$