

Monographs for Teachers

These popular publications present concise and authoritative accounts of selected but well-defined topics in chemistry for the guidance of teachers and students for further and higher education. All titles are paperbound unless otherwise stated.

TITLES IN PRINT

- NO. 2 PRINCIPLES OF OXIDATION AND REDUCTION
40pp 0 85404 026 9 £4.00
- NO. 8 PRINCIPALS OF ATOMIC ORBITALS
51pp 0 85404 028 5 £3.00
- NO. 9 PRINCIPLES OF REACTION KINETICS (Revised 2nd Edition in SI Units)
80pp 0 85404 024 2 £8.00
- NO. 13 PRINCIPLES OF OSMOTIC PHENOMENA (2nd Edition)
74pp 0 85404 025 0 £3.50
- NO. 15 PHYSICO-CHEMICAL QUANTITIES AND UNITS (2nd Edition)
128pp 0 85404 009 9 £5.00
- NO. 16 CHEMICAL PROCESSING IN INDUSTRY
34pp 0 85404 007 2 £3.50
- NO. 17 AN INTRODUCTION TO BIOCHEMISTRY
116pp 0 85404 016 1 £4.50 (Hardcover edition £9.00)
- NO. 18 PRINCIPLES OF CRYSTAL CHEMISTRY
72pp 0 85404 017 X £4.00 (Hardcover edition £8.00)
- NO. 19 THE MOLECULAR BASIS OF ENTROPY AND CHEMICAL EQUILIBRIUM
72pp 0 85404 020 X £3.50 (Hardcover edition £7.00)
- NO. 21 MODERN ANALYTICAL METHODS
234pp 0 85186 759 6 £12.50
- NO. 22 PRINCIPLES OF PHOTOCHEMISTRY
70pp 0 85186 769 3 £4.50
- NO. 23 CHEMICAL ASPECTS OF ATOMIC NUCLEUS
115pp 0 85186 779 0 £4.50
- NO. 24 PRINCIPLES OF FREE RADICAL CHEMISTRY
83pp 0 85186 829 0 £4.50
- NO. 25 SOME ASPECTS OF TECHNOLOGICAL ECONOMICS
99pp 0 85186 879 7 £4.00
- NO. 26 ELEMENTS OF ORGANOMETALLIC CHEMISTRY
103pp 0 85186 909 2 £4.50
- NO. 27 THE HYDROGEN BOND
40pp 0 85186 991 X £4.50
- NO. 28 SOME ASPECTS OF BASIC POLYMER SCIENCE
64pp 0 85186 939 4 £4.50
- NO. 29 ION-EXCHANGE: INTRODUCTION TO THEORY AND PRACTICE
91pp 0 85186 969 6 £5.00
- NO. 30 MOLECULAR STRUCTURE: ITS STUDY BY CRYSTAL DIFFRACTION
57pp 0 85186 689 1 £4.00
- NO. 31 THE PRINCIPLES OF BIOINORGANIC CHEMISTRY
114pp 0 85186 679 4 £5.00
- NO. 32 AN INTRODUCTION TO ENZYME CHEMISTRY
88pp 0 85186 599 2 £4.50
- NO. 33 INORGANIC REACTION MECHANISMS
112pp 0 85186 128 8 £4.00

Further information on the above titles can be obtained from: The Marketing Department, The Royal Society of Chemistry, Burlington House, London W1V 0BN. Orders should be sent to: The Royal Society of Chemistry, Distribution Centre, Blackhorse Road, Letchworth, Herts., SG6 1HN.

ROYAL
SOCIETY OF
CHEMISTRY

LINEAR FREE ENERGY RELATIONSHIPS

Peter Sykes



ETSG

CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

General Editor:

Peter Groves

The University of Aston in Birmingham

Published 1981 by the Educational Techniques Subject Group, The Royal Society of Chemistry, London.

© Peter Sykes 1981

ISBN 0 85186 378 7

All Chemistry Cassette materials are copyright and the tape recording and book may not be copied or reproduced in any way without the written permission of the Educational Techniques Subject Group. The materials are sold on the express condition that they are to be used for educational purposes only. They may not be used for commercial gain or be hired out for this or any other purpose without the prior written permission of the Educational Techniques Subject Group.

The views expressed in the recording and the book are those of the author and not necessarily those of the Royal Society of Chemistry.

Produced by Tetradon Publications Ltd., Warley, West Midlands.

Printed in the University of Aston in Birmingham

Please read this carefully before you start.

USING THE CHEMISTRY CASSETTE

This Chemistry Cassette learning programme has two components - an audio-cassette and this book. The two are designed to be used together so always have the book with you as you work through the cassette.

As you listen you will, from time to time, be asked to switch off your tape player and answer some questions. You should, therefore, have pen and paper ready before you start.

The material in the book consists of reaction schemes, figures and equations, each of which is clearly numbered. Dr Sykes will refer you to the appropriate number whenever he wishes you to locate a particular scheme and to study its contents. Because some of the questions asked are answered in subsequent schemes you should use a piece of paper or card to cover any schemes beyond the one that is being currently referred to.

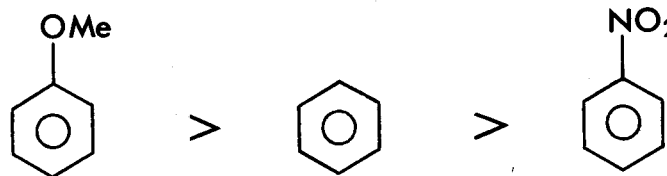
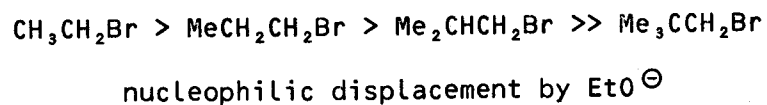
In addition to the schemes in the book a separate pull-out sheet with schemes 10 and 13 on it is also provided. You will be referred back to these on several occasions.

This programme has been designed for individual, self-paced learning and you can work through it at a rate related to your own needs and understanding. Switch off the tape player whenever you want to think, to write some notes or to answer a question. Use the rewind control to revise or to repeat material that you might not fully understand on a first hearing. Whenever appropriate make notes to supplement the material contained in the book; this will enable you to build up a detailed set of personal notes which will serve as your own authoritative guide to the subject.

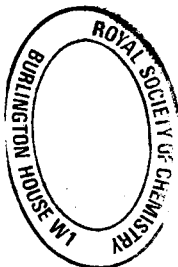
ACKNOWLEDGEMENTS

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.

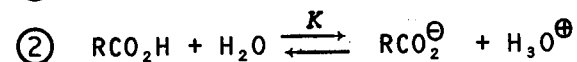
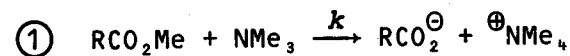
Linear Free Energy Relationships



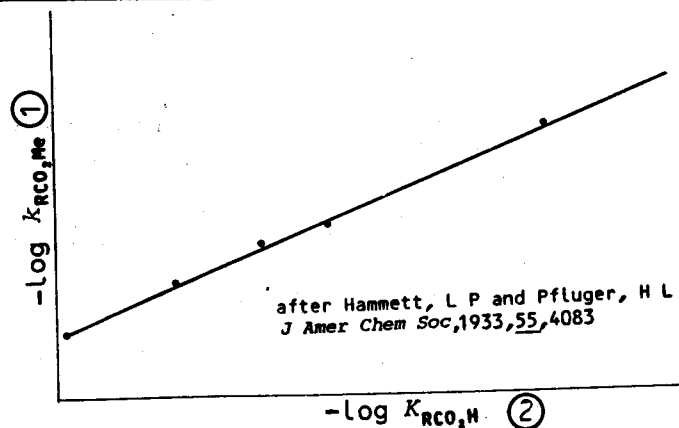
electrophilic "displacement" by NO_2^\oplus (nitration)



1 RELATIVE REACTIVITY SERIES



2 FIRST MAJOR STRUCTURE/REACTIVITY CORRELATION



3 STRAIGHT LINE PLOT: $-\text{LOG } k_{\text{RCO}_2\text{H}}$ (1) v. $-\text{LOG } k_{\text{RCO}_2\text{Me}}$ (2)

$$\Delta G^{\circ} = -2.303RT \log K$$

equilibrium constant

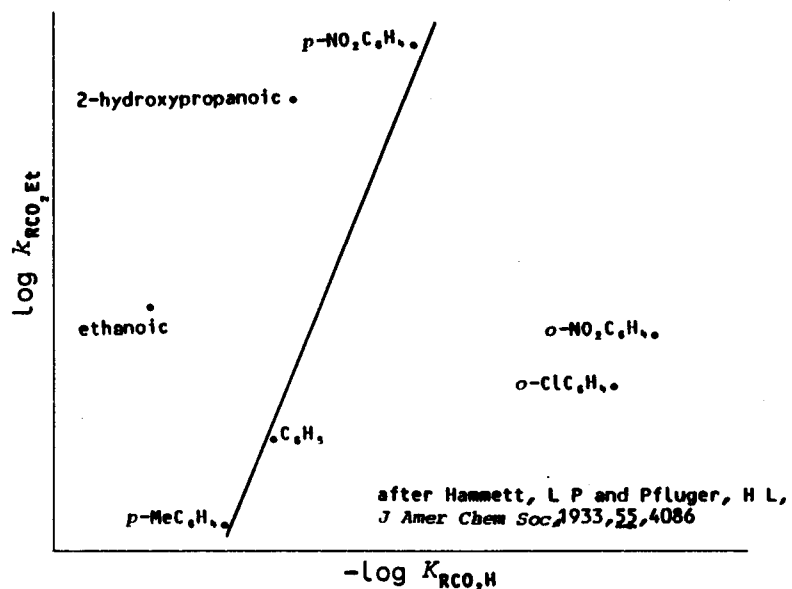
$$\Delta G^{\ddagger} = -2.303RT \log k \left[\frac{h}{kT} \right]$$

rate constant

k^{\ddagger} = Boltzmann constant
 h = Planck constant

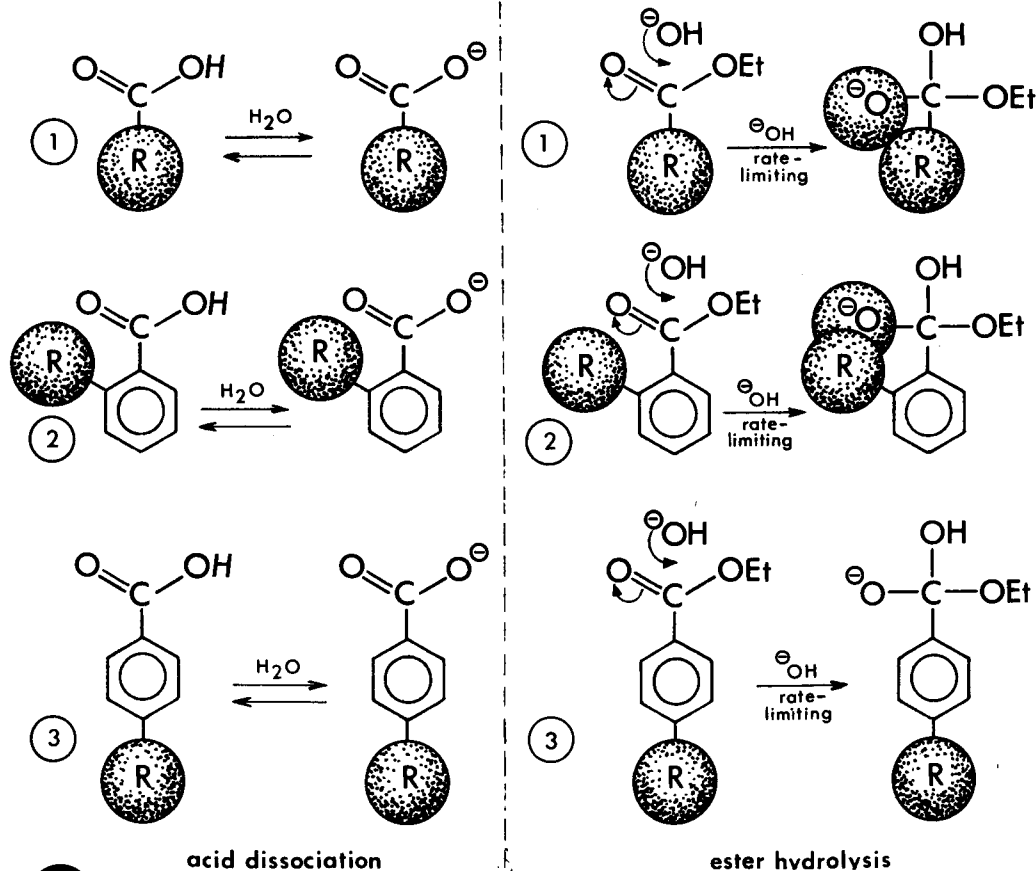
4

RELATIONSHIP BETWEEN K , k AND ΔG



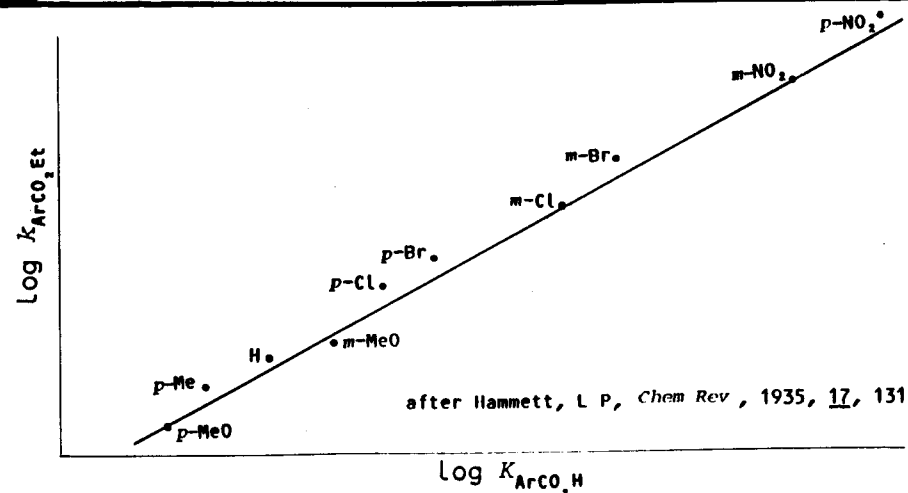
5

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):

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

where ρ 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, ie where $X = H$:

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

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

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

which may also be written in the form:

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

8

DERIVATION OF HAMMETT RELATION: (1)

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

$$\text{ie } \log \frac{K_{p-\text{NO}_2}}{K_H} = \sigma_{p-\text{NO}_2}, \quad \log \frac{K_{m-\text{Me}}}{K_H} = \sigma_{m-\text{Me}}$$

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

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

This is the most common representation of the Hammett relation.

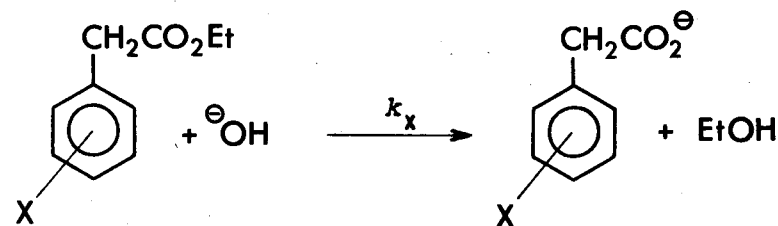
9

DERIVATION OF HAMMETT RELATION: (2)

Substituent, X	σ_{m-X}	σ_{p-X}
Me ₃ C	-0.10	-0.20
Me	-0.07	-0.17
H	0.00	0.00 (by definition)
MeO	+0.12	-0.27
HO	+0.12	-0.37
F	+0.34	+0.06
Cl	+0.37	+0.23
MeCO	+0.38	+0.50
Br	+0.39	+0.23
CN	+0.56	+0.66
NO ₂	+0.71	+0.78

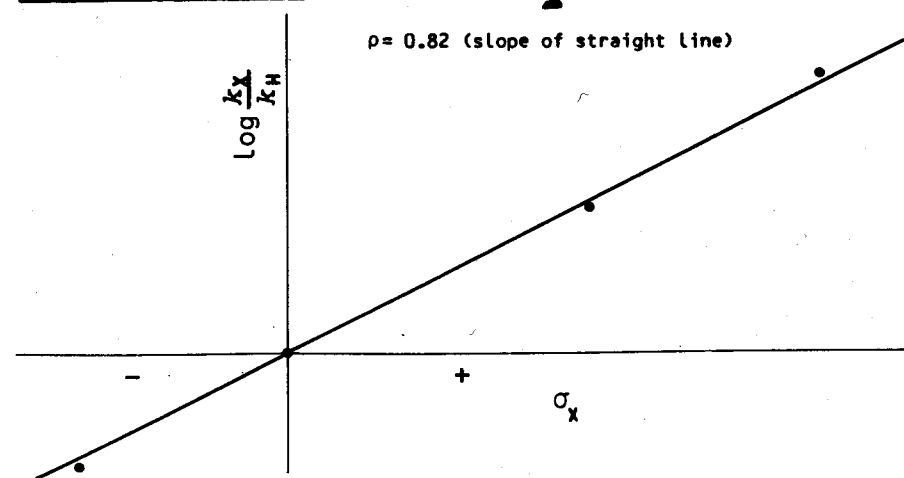
10

SOME SUBSTITUENT CONSTANT, σ_X , VALUES



11

BASE-CATALYSED HYDROLYSIS OF 2-ARYLETHANOATES

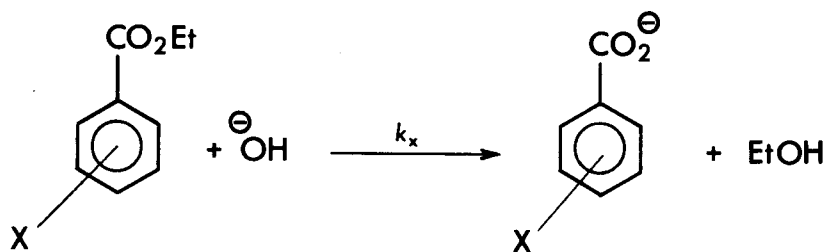


12

PLOT OF $\log \frac{k_X}{k_H}$ v. σ_X FOR 2-ARYLETHANOATE HYDROLYSIS

Reaction	Type	ρ
1) ArNH_2 with $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Cl}$ in EtOH (25°)	k	-3.19
2) ArNH_2 with $\text{C}_6\text{H}_5\text{COCl}$ in C_6H_6 (25°)	k	-2.69
3) ArCH_2Cl solvolysis in aq. Me_2CO (69.8°)	k	-1.88
4) ArO^\ominus with EtI in EtOH (25°)	k	-0.99
5) ArCO_2H with MeOH (acid-catalysed, 25°)	k	-0.09
6) ArCO_2Me hydrolysis (acid) in aq. MeOH (25°)	k	+0.03
7) $\text{ArCH}_2\text{CO}_2\text{H}$ dissociation in H_2O (25°)	K	+0.47
8) ArCH_2Cl with I^\ominus in Me_2CO (20°)	k	+0.79
9) $\text{ArCH}_2\text{CO}_2\text{Et}$ hydrolysis (base) in aq. EtOH (30°)	k	+0.82
10) ArCO_2H dissociation in H_2O (25°)	K	+1.00 (standard)
11) ArOH dissociation in H_2O (25°)	K	+2.01
12) ArCN with H_2S (base) in EtOH (60.6°)	k	+2.14
13) ArCO_2Et hydrolysis (base) in aq. EtOH (25°)	k	+2.51
14) ArNH_3^\oplus dissociation in H_2O (25°)	K	+2.73

13

SOME REACTION CONSTANT, ρ , VALUES

when $X = m\text{-NO}_2$: ① $\frac{k_{m\text{-NO}_2}}{k_{\text{H}}} = 63.5$

when $X = p\text{-MeO}$: ② $\frac{k_{p\text{-MeO}}}{k_{\text{H}}} = ?$

14

BASE-CATALYSED HYDROLYSIS OF $\text{XC}_6\text{H}_4\text{CO}_2\text{Et}$

$$\textcircled{1} \quad \log \frac{k_{m\text{-NO}_2}}{k_{\text{H}}} = \rho \sigma_{m\text{-NO}_2}$$

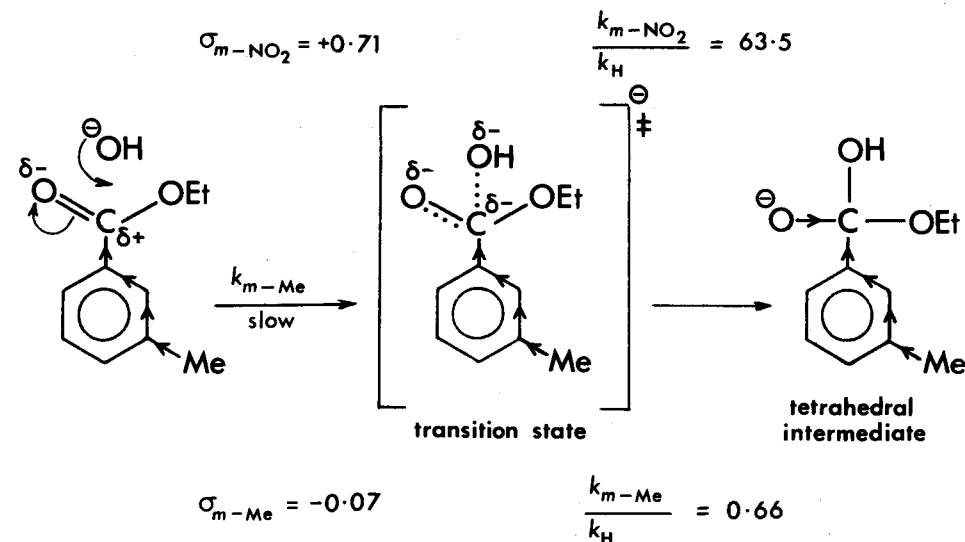
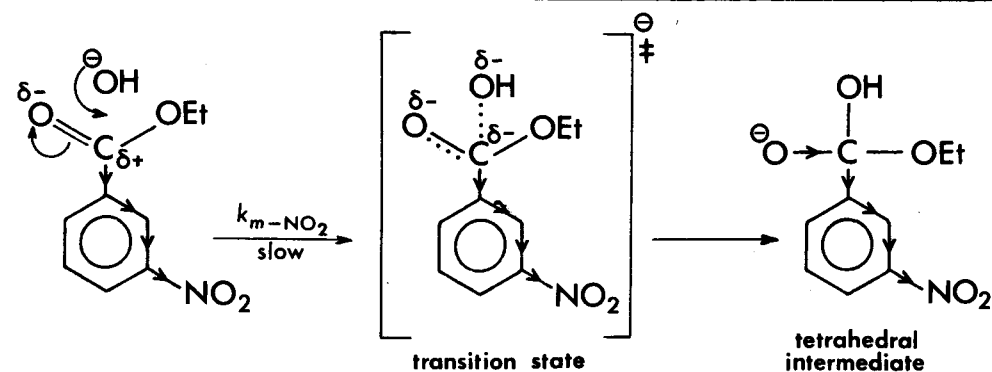
i.e. $\log \frac{63.5}{1} = \rho \times 0.71 \quad \therefore \rho = 2.54$

$$\textcircled{2} \quad \log \frac{k_{p\text{-MeO}}}{k_{\text{H}}} = \rho \sigma_{p\text{-MeO}}$$

i.e. $\log \frac{k_{p\text{-MeO}}}{k_{\text{H}}} = 2.54 \times -0.27 \quad \therefore \frac{k_{p\text{-MeO}}}{k_{\text{H}}} = 0.21$

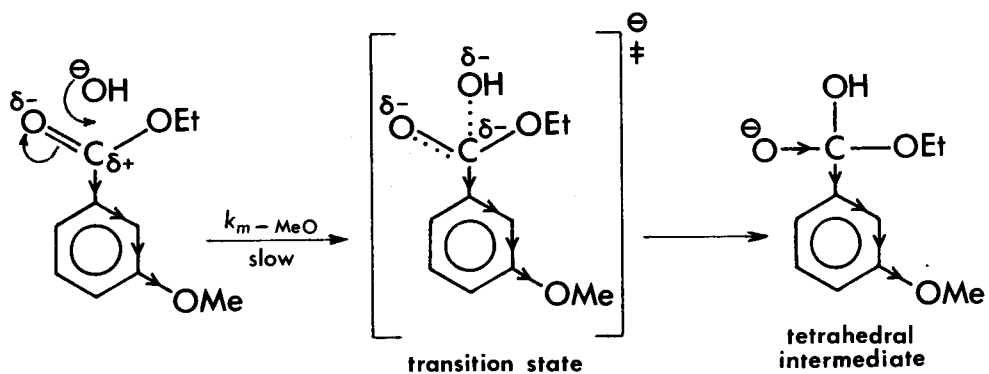
15

CALCULATION OF RELATIVE REACTION RATE



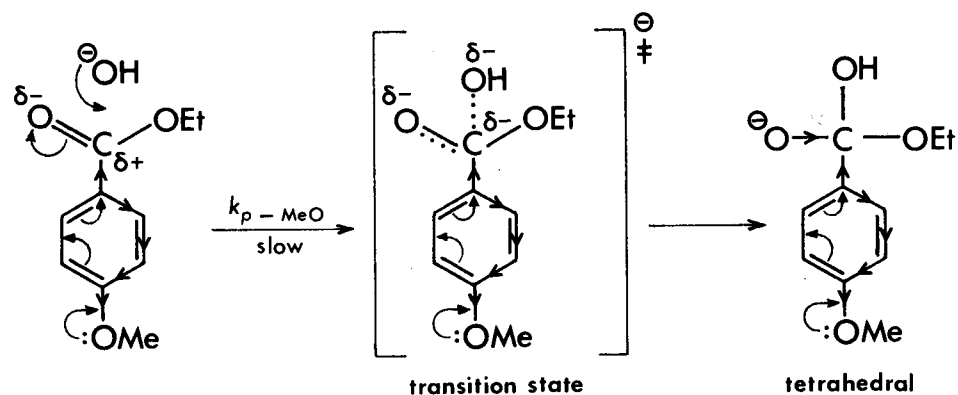
16

EFFECT OF m -SUBSTITUENTS ON ESTER HYDROLYSIS



$$\sigma_{m-\text{MeO}} = +0.12$$

$$k_{m-\text{MeO}} > k_{\text{H}}$$

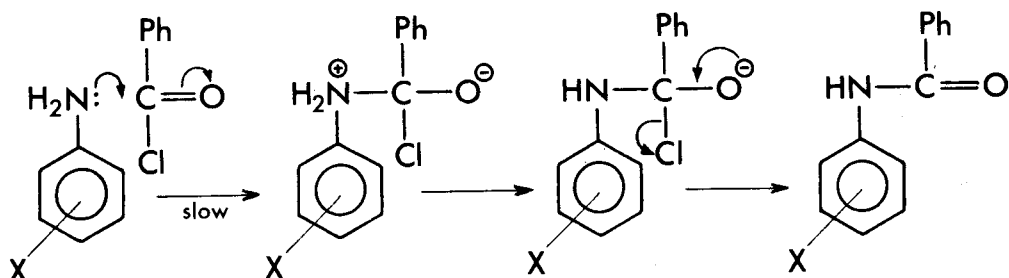


$$\sigma_{p-\text{MeO}} = -0.27$$

$$k_{\text{H}} > k_{p-\text{MeO}}$$

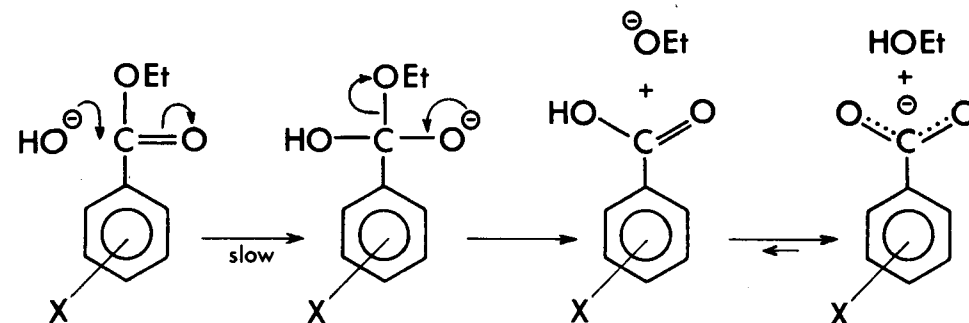
17

EFFECT OF *m*- or *p*-MeO ON ESTER HYDROLYSIS



18

BENZOYLATION OF $\text{XC}_6\text{H}_4\text{NH}_2$: $\rho = -2.69$



19

BASE-CATALYSED HYDROLYSIS OF $\text{XC}_6\text{H}_4\text{CO}_2\text{Et}$: $\rho = +2.51$

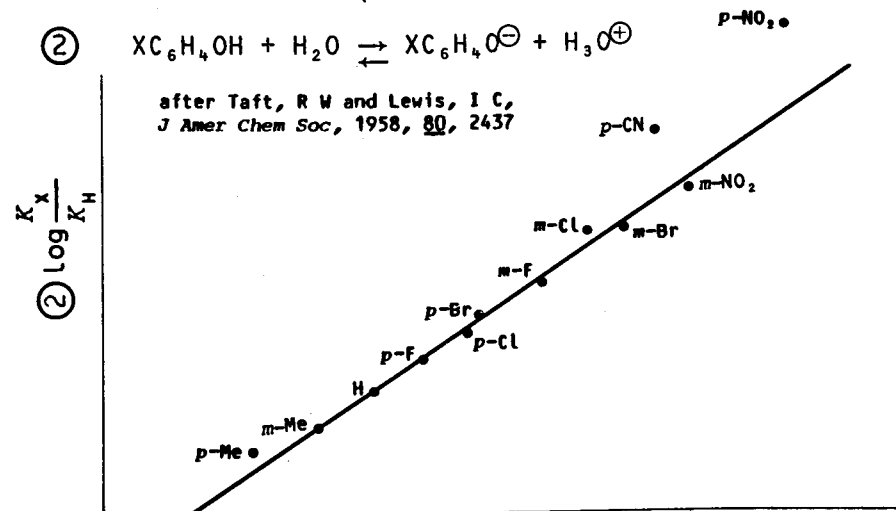
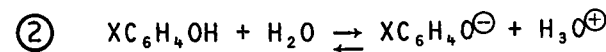
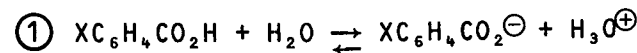
Acid dissociation (H_2O)

ρ

$\text{XC}_6\text{H}_4\text{CO}_2\text{H}$	1.00 (standard reaction)
$\text{XC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$	0.49
$\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	0.21
$\text{XC}_6\text{H}_4\text{CH}=\text{CHCO}_2\text{H}$	0.47

20

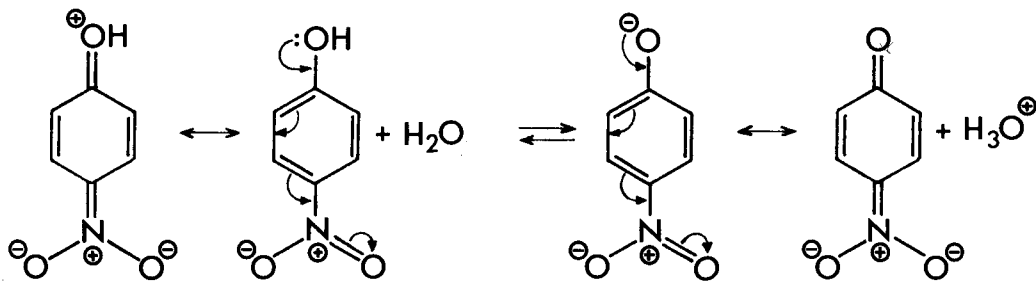
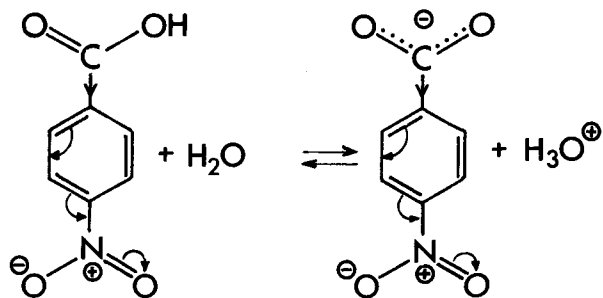
ρ VALUES FOR DISSOCIATION OF $\text{XC}_6\text{H}_4\text{CO}_2\text{H}$



① $\log \frac{K_x}{K_H}$

21

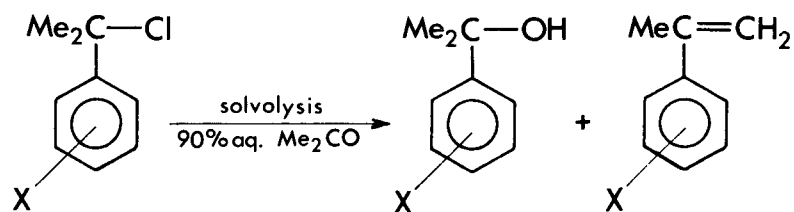
COMPARISON OF AQUEOUS DISSOCIATIONS OF $\text{XC}_6\text{H}_4\text{CO}_2\text{H}$ AND $\text{XC}_6\text{H}_4\text{OH}$



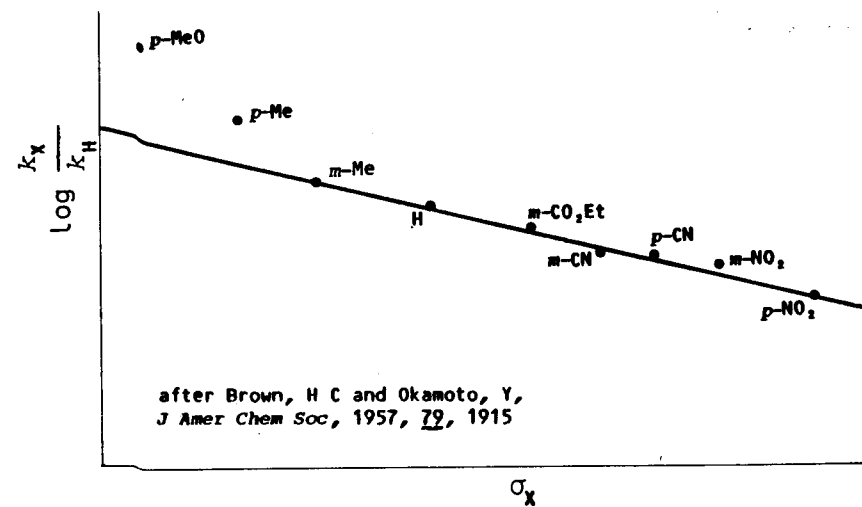
22 ELECTRONIC EFFECTS IN $p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ AND $p\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$ DISSOCIATIONS

Substituent, X	σ_{p-X}^-	σ_{p-X}
CO_2Et	0.68	0.45
COMe	0.84	0.50
CN	0.88	0.66
CHO	1.03	0.43
NO_2	1.27	0.78

23 σ_X^- v. σ_X FOR SOME ELECTRON-WITHDRAWING p -SUBSTITUENTS

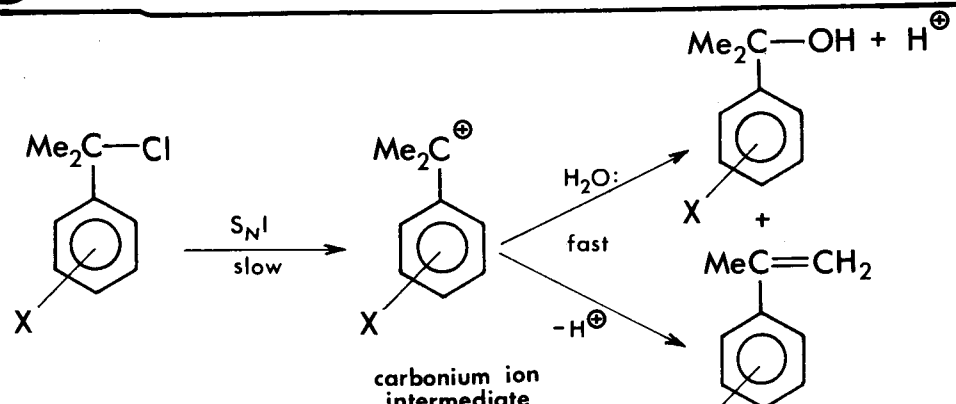


24 SOLVOLYSIS OF $\text{XC}_6\text{H}_4\text{CMe}_2\text{Cl}$

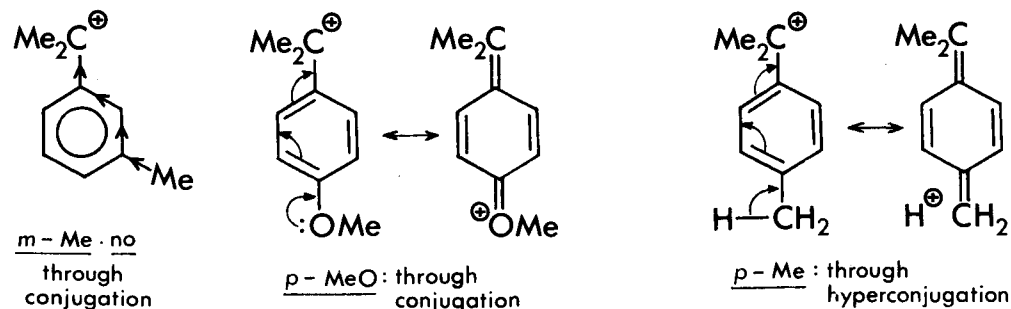


after Brown, H C and Okamoto, Y,
J Amer Chem Soc, 1957, 79, 1915

25 $\text{LOG} \frac{k_X}{k_H}$ v. σ_X FOR SOLVOLYSIS OF $\text{XC}_6\text{H}_4\text{CMe}_2\text{Cl}$



26 S_N1 SOLVOLYSIS OF $\text{XC}_6\text{H}_4\text{CMe}_2\text{Cl}$



$m\text{-Me}$: no
through
conjugation

$p\text{-MeO}$: through
conjugation

$p\text{-Me}$: through
hyperconjugation

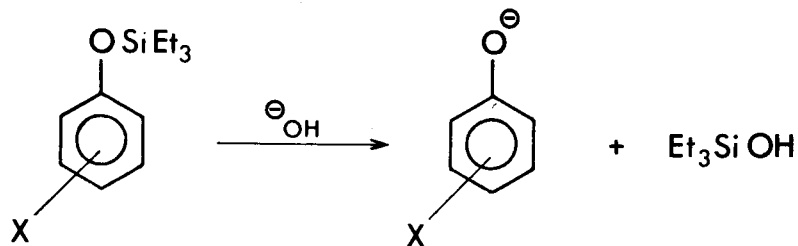
27 THROUGH CONJUGATION WITH ELECTRON-DONATING p -SUBSTITUENTS

Substituent, X	σ_{p-X}^+	σ_{p-X}
C ₆ H ₅	-0.18	-0.01
Me	-0.31	-0.17
MeO	-0.78	-0.27
NH ₂	-1.30	-0.66
NMe ₂	-1.70	-0.83

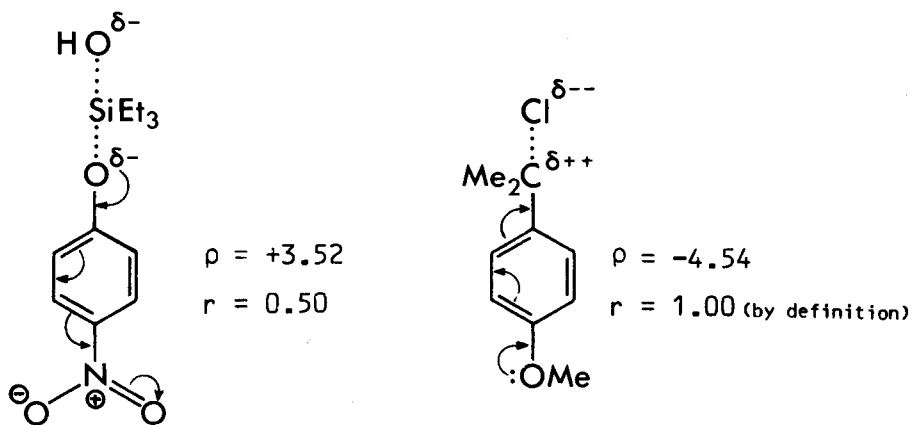
28 σ_x^+ v. σ_x FOR SOME ELECTRON-DONATING p-SUBSTITUENTS

$$\log \frac{k_x}{k_H} = \rho[\sigma_x + r(\sigma_x^+ - \sigma_x)] \quad \dots [7]$$

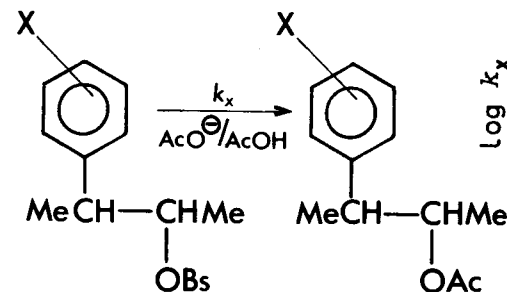
29 YUKAWA-TSUNO RELATION



30 BASE-CATALYSED HYDROLYSIS OF XC₆H₄OSiEt₃

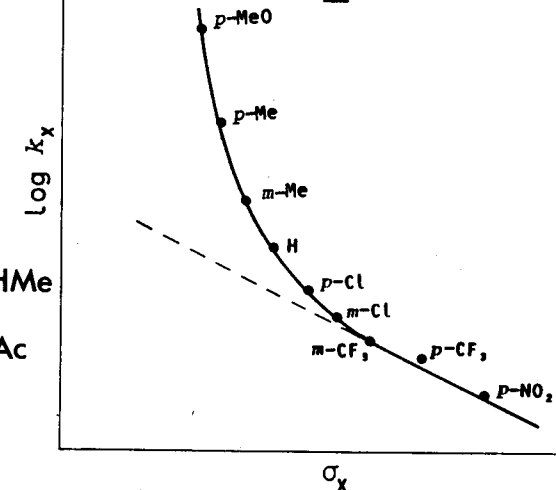


31 TRANSITION STATES IN WHICH THROUGH CONJUGATION OPERATES

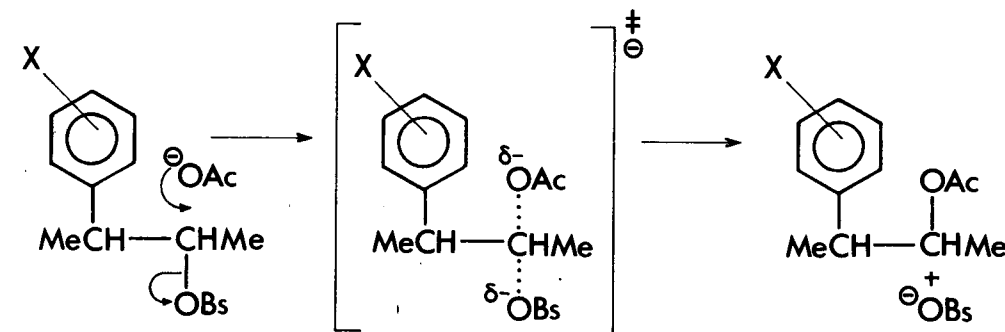


[Bs = p-BrC₆H₄SO₂]

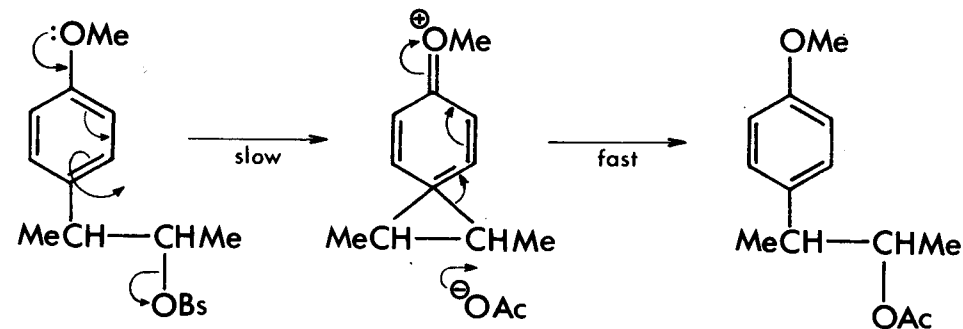
after Brown, H C, Schleyer P von R et al, J Amer Chem Soc, 1970, 92, 5244



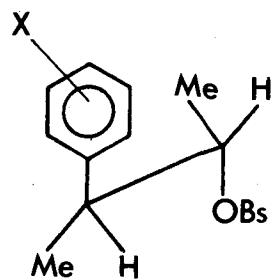
32 ACETOLYSIS OF 3-ARYL-2-BUTYL BROSYLATES



33 S_N2 ACETOLYSIS OF 3-ARYL-2-BUTYL BROSYLATES

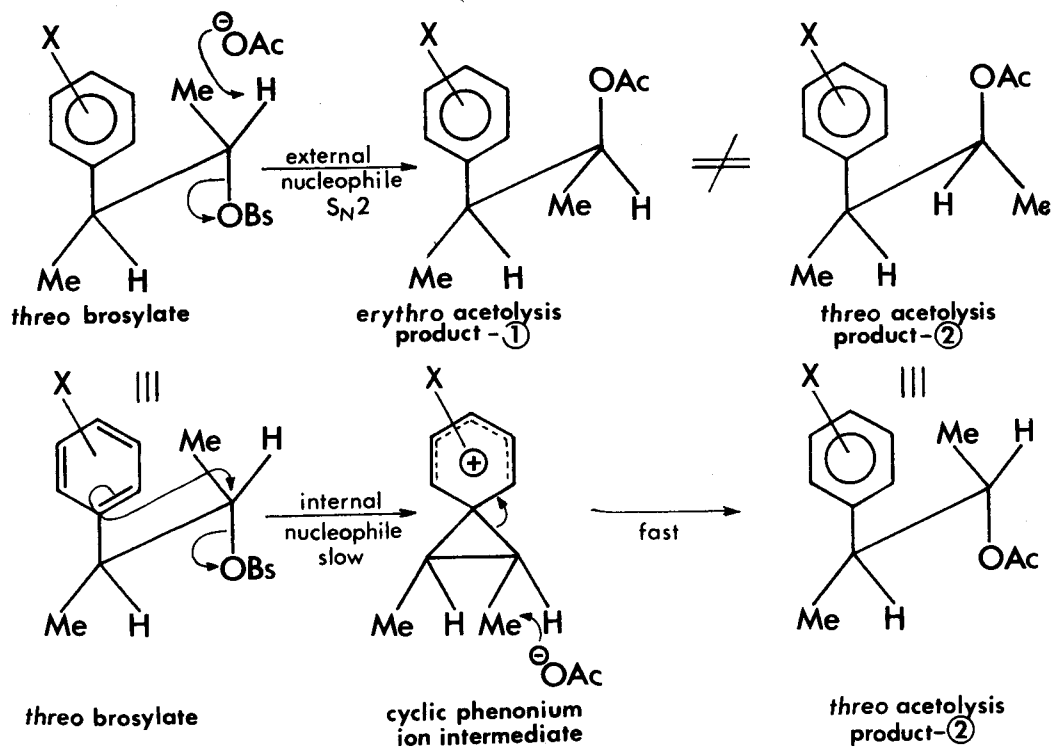


34 XC₆H₄ AS AN INTERNAL NUCLEOPHILE



35

THREO 3-ARYL-2-BUTYL BROSYLATES



36

DISTINGUISHABLE PRODUCTS FROM EXTERNAL AND INTERNAL NUCLEOPHILIC ATTACK

Substituent, X

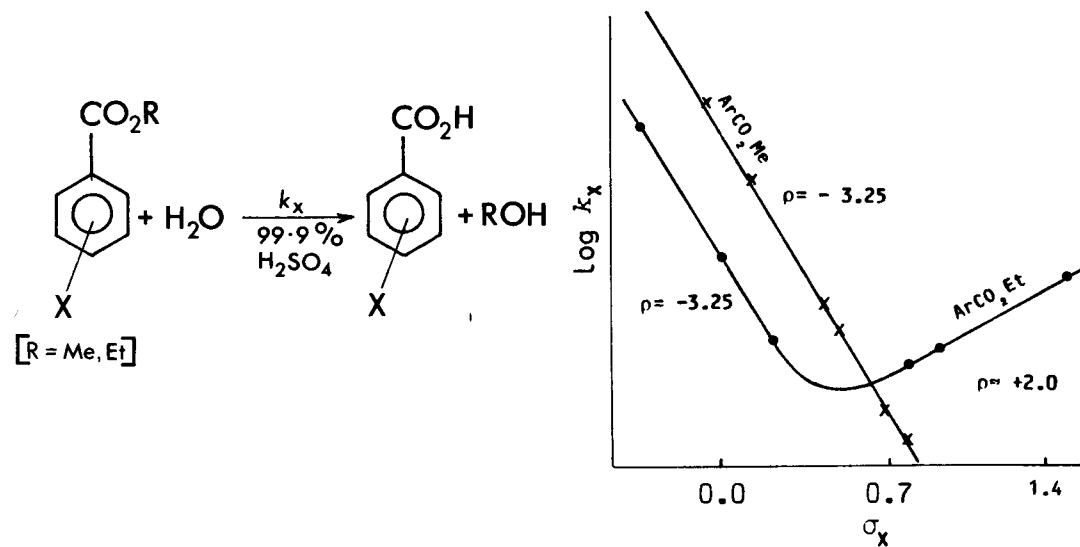
Yield of *threo* product - ②*

<i>p</i> -MeO	100%
<i>p</i> -Me	88%
<i>m</i> -Me	68%
H	59%
<i>p</i> -Cl	39%
<i>m</i> -Cl	12%
<i>m</i> -CF ₃	6%
<i>p</i> -NO ₂	1%

* = % of reaction proceeding by internal attack

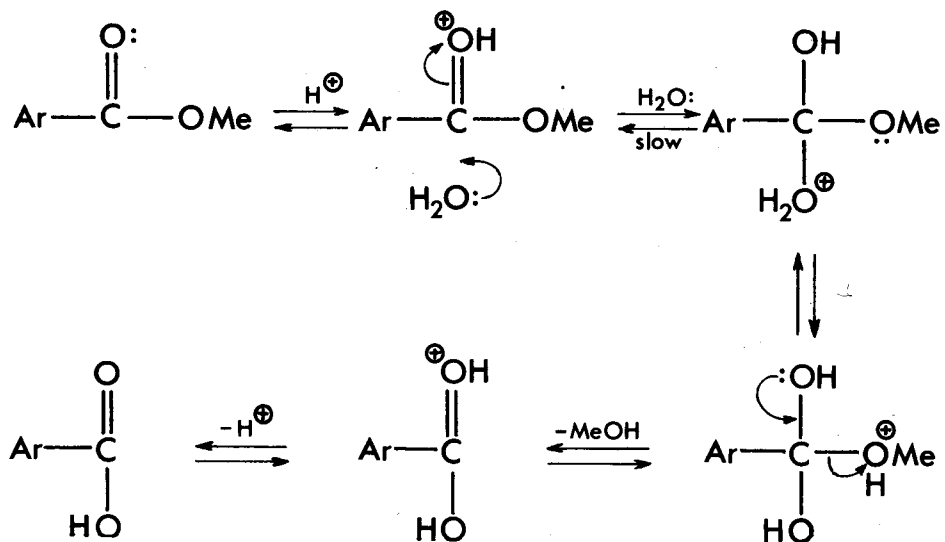
37

VARIATION IN YIELD OF THREO PRODUCT - ② WITH SUBSTITUENT, X

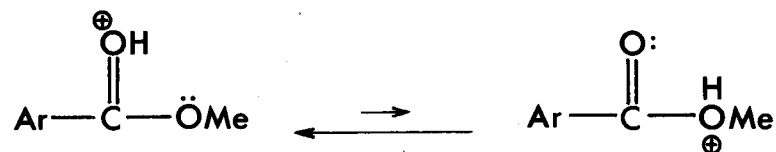


38

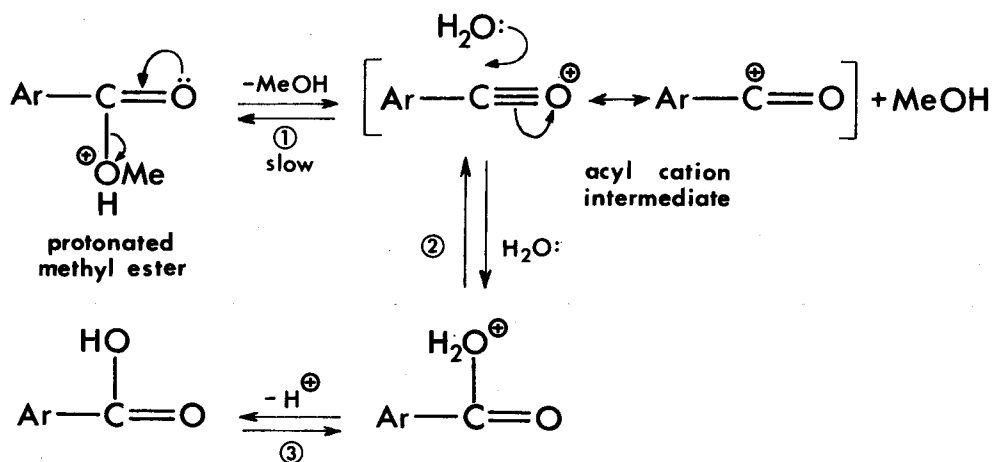
HYDROLYSIS OF XC₆H₄CO₂R IN 99.9% H₂SO₄



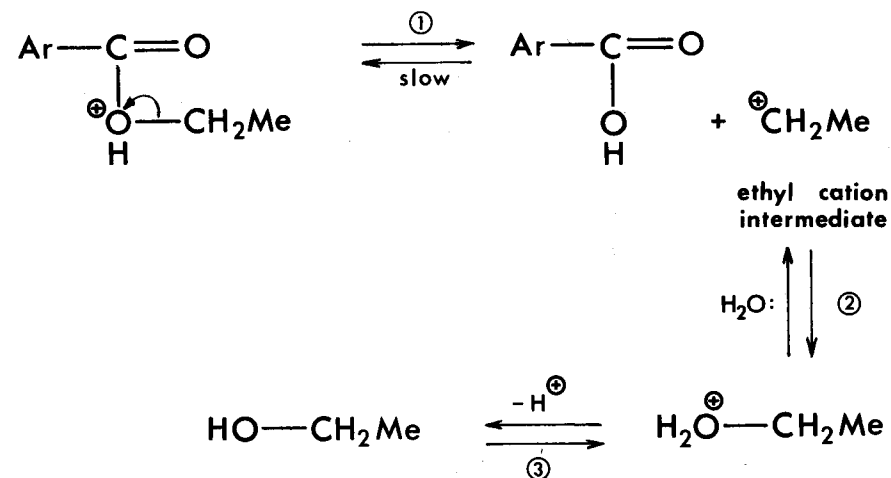
39 ACID-CATALYSED ESTER HYDROLYSIS - COMMON (A_{AC}2) PATHWAY



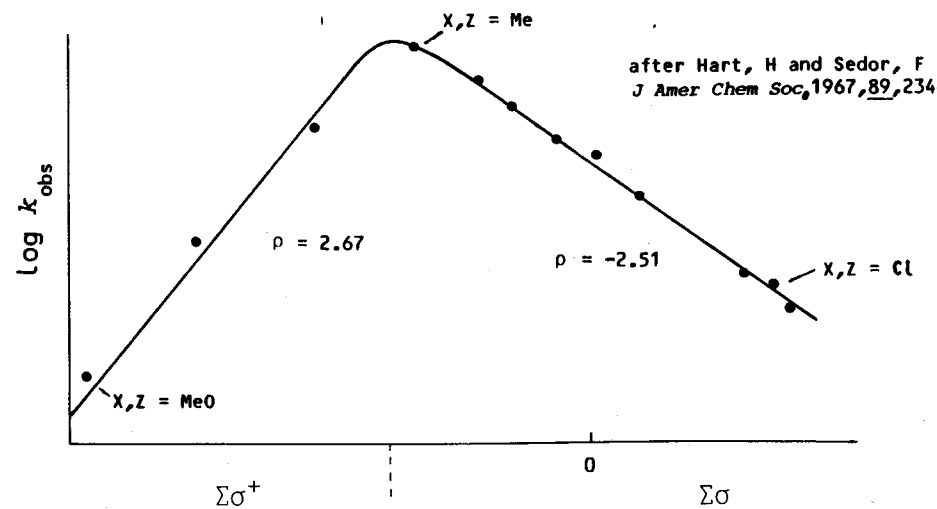
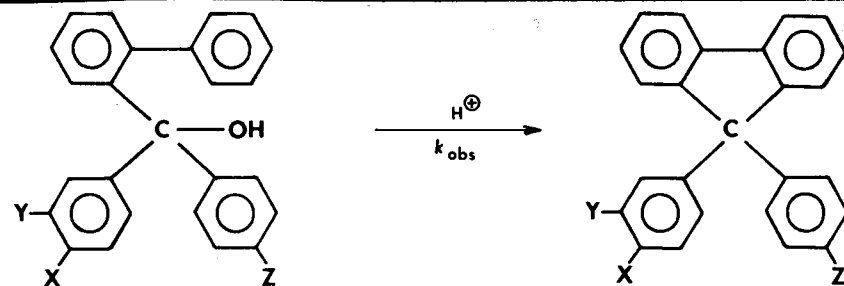
40 POSSIBLE TAUTOMERIC EQUILIBRIUM IN PROTONATED METHYL ESTER



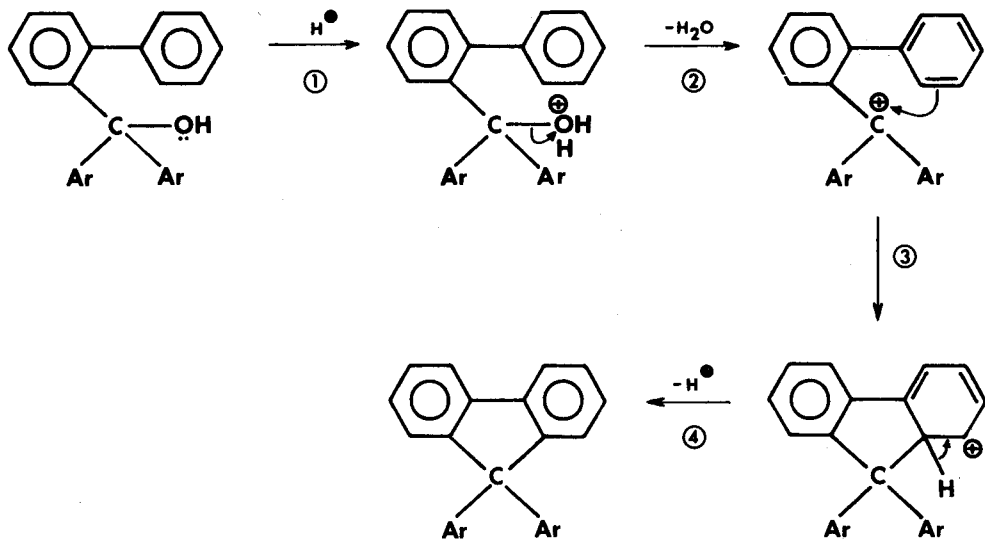
41 ACID-CATALYSED ESTER HYDROLYSIS - A_{AC}1 PATHWAY



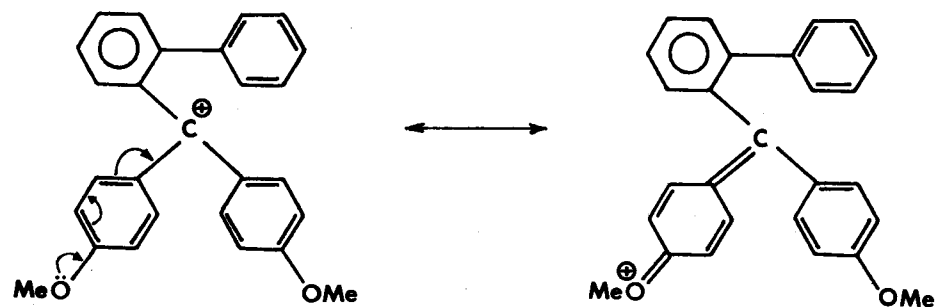
42 ACID-CATALYSED ESTER HYDROLYSIS - A_{AL}1 PATHWAY



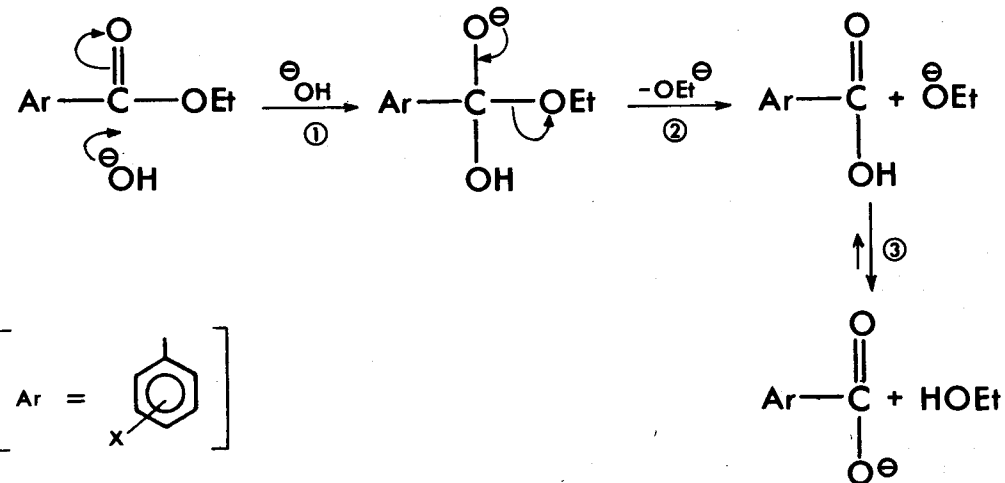
43 CYCLODEHYDRATION OF 2-PHENYLTRIARYLMETHANOLS



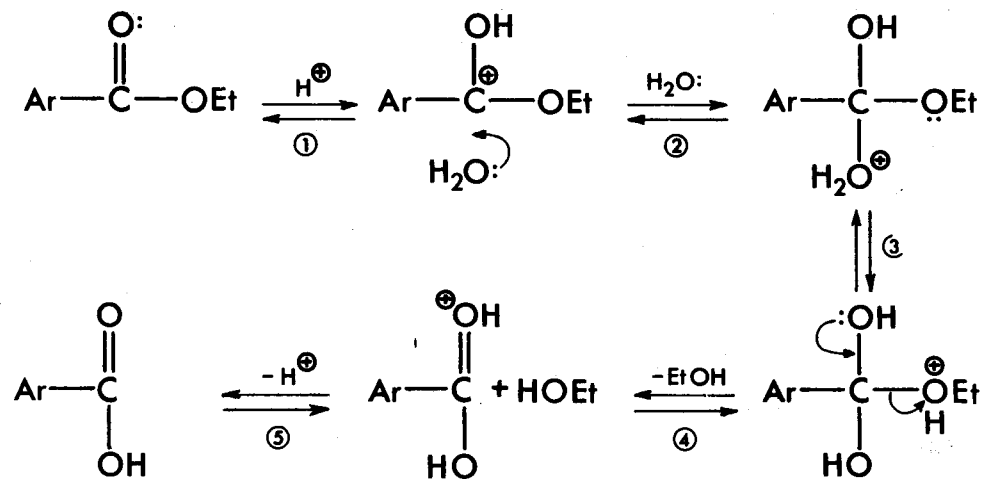
44 CYCLODEHYDRATION AS DEHYDRATION/INTERNAL ELECTROPHILIC SUBSTITUTION



45 STABILISATION OF CARBONIUM ION INTERMEDIATE FROM ALCOHOL WITH X = Z = OMe

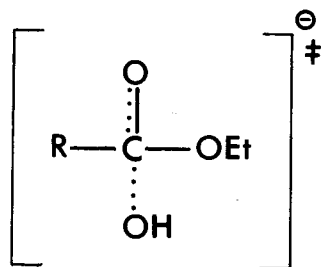


Base-catalysed hydrolysis (B_{AC}2): ρ = 2.51

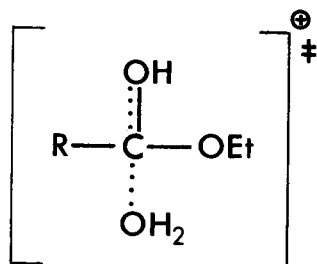


Acid-catalysed hydrolysis (A_{AC}2): ρ = 0.03

46 BASE (B_{AC}2) AND ACID (A_{AC}2) CATALYSED ESTER HYDROLYSIS



T.S. for base-catalysed hydrolysis ($B_{AC}2$)



T.S. for acid-catalysed hydrolysis ($A_{AC}2$)

47 TRANSITION STATES FOR $B_{AC}2$ AND $A_{AC}2$ ESTER HYDROLYSIS

$$\log \left[\frac{k_R}{k_0} \right]_{\text{base}} - \log \left[\frac{k_R}{k_0} \right]_{\text{acid}} = \rho^* \sigma_R^* \quad \dots [8]$$

48 EQUATION FOR OPERATION OF POLAR EFFECTS ONLY IN ESTER HYDROLYSIS

$$\log \frac{k_R}{k_{Me}} = \rho^* \sigma_R^* \quad \dots [9]$$

GENERALISED TAFT POLAR EFFECT EQUATION

49

$$\log \left[\frac{k_{RCO_2Et}}{k_{MeCO_2Et}} \right]_{\text{acid}} = E_s \quad \dots [10]$$

EVALUATION OF STERIC PARAMETER, E_s

50

R in RCO_2Et	E_s
H	+1.24
Me	0 (by definition)
Et	-0.07
$ClCH_2$	-0.24
ICH_2	-0.37
$PhCH_2$	-0.38
$Me(CH_2)_3$	-0.39
Me_2CHCH_2	-1.13
Me_3C	-1.54
Me_3CCH_2	-1.74
Ph_2CH	-1.76
Et_3C	-3.81

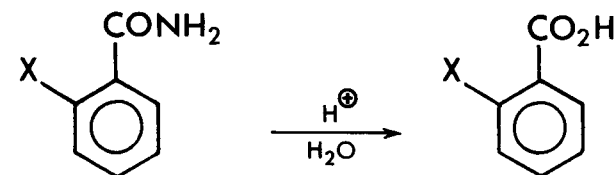
E_s VALUES FOR R IN RCO_2Et

51

$$\log \frac{k_R}{k_{Me}} = \rho^* \sigma_R^* + \delta E_s \quad \dots [11]$$

INCORPORATION OF VARIABLE STERIC PARAMETER, δE_s

52



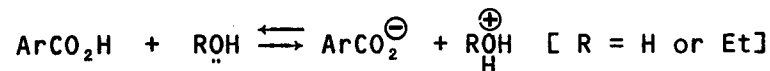
ACID-CATALYSED HYDROLYSIS OF o-SUBSTITUTED BENZAMIDES

53

Reaction	ρ
$\text{ArCO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{ArCO}_2^- + \text{H}_3\text{O}^+(\text{H}_2\text{O})$	1.00 (by definition)
" " \rightleftharpoons " " (50% aq. EtOH)	1.60
" " \rightleftharpoons " " (EtOH)	1.96
$\text{ArCO}_2\text{Et} + \ominus\text{OH} \rightarrow \text{ArCO}_2^- + \text{EtOH}$ (70% aq. dioxan)	1.83
" " \rightarrow " " (85% aq. EtOH)	2.54

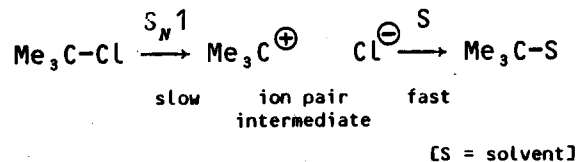
54

VARIATION OF ρ WITH SOLVENT



55

DISSOCIATION OF ArCO_2H IN HYDROXYLIC SOLVENTS



$$\log k_A - \log k_0 = Y_A - Y_0 \quad \dots [12]$$

56

GRUNWALD-WINSTEIN: STANDARD REACTION AND EQUATION

Solvent, A	Y_A
H ₂ O	+3.49
aq. MeOH (50% H ₂ O)	+1.97
HCONH ₂	+0.60
aq. EtOH (30% H ₂ O)	+0.59
aq. EtOH (20% H ₂ O)	0.00 (by definition)
aq. Me ₂ CO (20% H ₂ O)	-0.67
MeOH	-1.09
EtOH	-2.03
Me ₂ CHOH	-2.73
Me ₃ COH	-3.26

57

SOLVENT PARAMETER, Y_A , VALUES

$$\log \frac{k_A}{k_0} = mY_A \quad \dots [13]$$

58

GRUNWALD-WINSTEIN EQUATION

Halide	m
PhCH(Me)Br	1.20
Me ₃ CCl	1.00 (by definition)
Me ₃ CBr	0.94
EtMe ₂ CBr	0.90
CH ₂ =CHCH(Me)Cl	0.89
EtBr	0.34
Me(CH ₂) ₃ Br	0.33

59

SUBSTRATE PARAMETER, m , VALUES

