[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Linear Free Energy Relationships from Rates of Esterification and Hydrolysis of Aliphatic and Ortho-substituted Benzoate Esters

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The reactivity of *o*-monosubstituted benzoate and aliphatic esters toward esterification and hydrolysis can be described approximately, within the limits indicated, by Eq. (1), log $k/k_0 = fA$. A is a substituent constant, f a reaction constant, and k/k_0 the relative rate for such an ester (or acid) in a given reaction series. Equation (1) is much more limited than the Hammett eq., log $k/k_0 = \sigma\rho$, which has been applied to many reactions of *m*- and *p*-substituted benzene derivatives. This is shown by the following facts: (1) Eq. (1) is limited to esterification and hydrolysis reactions; (2) the substituent constant, A, for *o*-substituted benzoate or aliphatic esters depends upon whether the reaction is catalyzed by acid or base, or upon whether structure is varied in the acyl or alkyl component of the ester. That is, four different parameters are required for a given substituent, one for each of these four conditions; (3) values of the substituent constant, A, bear no apparent relationship to the English school theory of polarity of substituent groups; (4) Eq. (1) fails to apply to both rate and equilibrium (*i.e.*, for example, to both rates of ester hydrolysis and the ionization constants of corresponding carboxylic acids). The fact that Eq. (1) permits such pronounced solvent variation as from pure alcohols to water with very slight effect on the reaction constant, f, demonstrates that for these reactions relative rates are nearly independent of solvent. Other factors affecting f are discussed.

Two very important relationships have been established which relate structure to rate and equilibrium. These are the Brönsted catalysis law and the Hammett equation.[1] Both of these relationships give linear free energy plots between rate and equilibrium within wide limits of structure variation. In the latter case, linear log–log relationships exist (among others) between rates of reactions of meta- and para-substituted benzoates and the ionization equilibrium constants of the corresponding carboxylic acids. No such parallelism between rate and equilibrium exists, however, for ortho-substituted benzoates[2] or aliphatic esters (or aliphatic reactions in general).

Pfluger[3] has found that the comparison of the rates of two base-catalyzed reactions permits a wider range of variation in structure of the base catalyst than does the comparison of rate and equilibrium constants for a single reaction series. Grunwald and Winstein have found that alkyl halides and esters which appear to solvolyze by a rate-determining ionization give linear plots of the logarithm of the first order rate constants in various solvents against log k_1 for *t*-butyl chloride in the corresponding solvents.[4] These results, although disturbing from the point of view of rate *vs.* equilibrium, are very important in the study of the effect of structure on reactivity.

The present subject reports the existence of approximate linear free energy (L.F.E.) relationships[5] between rates of esterification and hydrolysis for those esters which do not follow the Hammett equation. These relationships for all of the data which could be found have been tabulated by relating the logarithm of the relative rate, k/k_0, (k_0 is rate constant for a given ester chosen as standard of comparison) for various reaction series to the same quantity for one series chosen as a standard of reference. This procedure has been used for both acid and base catalyzed reaction series in which structure is both varied in only the acyl or the alkyl component of the ester. The defining equation is[5]

$$\log k/k_0 = fA \qquad (1)$$

where f = proportionality constant, or free energy reaction constant, dependent only upon the nature of the reaction series; k = rate constant for any ester (or acid) in given reaction series; k_0 = rate constant for acetate or ethyl ester in given aliphatic reaction series, or for ortho-substituted benzoates, the rate constant for *o*-toluate ester (or acid) in a given reaction series; $A = \log k/k_0$ for the standard reaction series (for which $f \equiv 1$), a substituent constant dependent only upon the nature of substituent introduced so as to derive the given ester from the standard ester.

Values of A for various aliphatic substituents and ortho-substituted benzoates are given in Table I, together with n, the number of reactions for which data are available for each substituent, and r, the median deviation of the value of the substituent constant for these reactions. Free energy reaction constants, f, obtained by methods of least squares, the number of substituents, n, for which data are available, and r, the probable error of f, are listed for each reaction series in Table II.

The values of f are unity for reaction series 1, 2, 3 and 4 of Table II (part 1a) within the average probable error of the L.F.E. relationship. One may then, within the precision of this relationship define these four reaction series as the standard of comparison of acid-catalyzed reactions in which structure is varied in the acyl component. Similarly, reaction series 1, 2 and 4 of Table II (part 1b) may be regarded as the standard of comparison for base-catalyzed reactions in which structure is varied in the acyl component. Accordingly, the values of A for aliphatic substituents given in Table I were obtained in these two cases by averaging the values of log k/k_0 for the reaction series indicated. The use of average values appears desirable on the basis that small specific effects and experimental errors will be reduced. Insufficient data are at

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(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184-190, and 222.

(2) The term ortho-substituted will throughout refer to *mono* ortho-substituted.

(3) H. L. Pfluger, THIS JOURNAL, **60**, 1513 (1938).

(4) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(5) Note: The term linear free energy relationship is used to describe Eq. (1) because of the fact that log k/k_0 is proportional to the relative free energy of activation according to the transition state theory of reaction rates.

TABLE I

SUBSTITUENT CONSTANTS

ALIPHATIC SERIES

	Substituent in acyl component						Substituent in alkyl component					
	Acid-catalyzed			Base-catalyzed			Acid-catalyzed			Base-catalyzed		
Substituent	*A*	*n*	*r*	*A*	*n*	*r*	*A*	*n*	*r*	*A*	*n*	*r*
H–	+1.24	3	0.09	+2.46	5	0.12	....	..	....	....	..	..
CH_3–	0.00	5	.06	0.00	8	.08	0.00	2	0.02	0.00	8	0.06
C_2H_5–	– .07	4	.02	– .31	8	.05	– .09	2	.01	– .49	8	.04
$ClCH_2$–	– .19	3	.05	....	..	..	....	..	....	....	..	..
n-C_3H_7–	– .36	4	.02	– .64	8	.09	.00	1	....	– .67	7	.06
n-C_4H_9–	– .39	4	.05	– .71	4	.09	....	..	...	– .73	7	.06
n-C_5H_{11}–	– .40	3	.07	– .55	2	.02	....	..	....	....	..	..
i-C_5H_{11}	– .35	2	.01	....	..	..	....	..	....	– .88	1	..
$C_6H_5CH_2$–	– .38	3	.04	+ .17	2	.03	– .25	2	.05	– .25	3	.06
$C_6H_5CH_2CH_2$–	– .43	3	.09	– .14	2	.01	....	..	....	– .51	2	.08
$C_6H_5CH_2CH_2CH_2$–	– .45	2	.06	– .40	2	.02	....	..	....	....	..	..
i-C_3H_7–	– .47	4	.06	– .94	7	.08	– .42	2	.03	–1.29	8	.05
Cyclo-C_6H_{11}–	– .79	2	.17	....	..	..	....	..	....	–1.53	1	..
i-C_4H_9–	– .93	3	.10	–1.24	3	.06	– .23	1	....	–0.81	1	..
Cyclo-$C_6H_{11}CH_2$–	– .98	3	.05	–1.13	1	..	....	..	....	....	..	..
(Me)(Et)CH–	–1.13	2	.16	....	..	..	....	..	....	–1.61	1	..
$(C_6H_5)(CH_3)CH$–	–1.19	2	.07	–0.93	1	..	....	..	....	....	..	..
$(C_6H_5)(C_2H_5)CH$–	–1.50	2	.10	–1.42	1	..	....	..	....	....	..	..
t-C_4H_9–	–1.54	3	.02	–2.38	7	.12	....	..	....	–2.83	3	.02
$(C_6H_5)_2CH$–	–1.76	3	.15	–1.09	1	..	....	..	....	....	..	..
$(C_2H_5)_2CH$–	–1.98	3	.28	–2.70	2	.06	....	..	....	....	..	..
$C_6H_5CH{=}CH$–	–1.99	1	..	–0.75	2	.09	....	..	....	....	..	..
Cl_3C–	–2.06	1	..	....	..	..	....	..	....	....	..	..
C_6H_5–	–2.55	3	.08	–1.06	3	.04	– .30	2	.01	+0.62	3	.06
CH_3OCH_2–	....	..	..	+1.10	4	.06	....	..	....	....	..	..
Cyclo-C_5H_9–	....	..	..	....	..	..	....	..	....	–1.36	1	..
$Me_2(Et)C$–	....	..	..	....	..	..	....	..	....	–3.25	1	..

Ortho-substituted benzoates

	Acid-catalyzed			Base-catalyzed		
Substituents	*A*	*n*	*r*	*A*	*n*	*r*
OCH_3	+1.11	2	0.04	+0.53	1	..
OC_2H_5	+1.01	2	.04	+ .53	1	..
CH_3	0.00	2	.06	.00	3	0.06
Cl	+ .09	2	.04	+1.11	3	.01
Br	– .06	2	.01	+0.94	3	.08
I	– .29	2	.01	+ .68	2	.04
NO_2	–1.07	2	.12	+1.70	3	.05
C_6H_5	....	..	..	–0.87	1	..

present available to use this procedure in obtaining all other substituent constants in Table I.

A close examination of the nature of the reaction series listed in Table II reveals that the reaction constants, *f*, are always positive and for most reactions near unity. The effect on *f* of solvent, of structure in the acyl and alkyl component, and of nature of the attacking reagent is summarized below.

Solvent.—In no case does the appropriate comparison show a reliable variation of *f* of greater than 20% for solvents ranging from pure water to mixed aqueous organic solvents to pure alcohols. The greatest variation of *f* with solvent appears for comparisons between pure water and the others, the value of *f* being smaller in the former. Considerable variation in aqueous organic solvents is permitted essentially without effect on *f*.

Structure.—In the acyl component, *f* shows a strong dependence upon structure. The largest variation of *f* in Table II is shown by reaction series of formate, acetate or propionate, *i*-butyrate and trimethylacetate esters under otherwise similar conditions. Values of *f* increase in the order given by an over-all factor of approximately four.

In the alkyl component, *f* depends only slightly upon structure. For *o*-substituted benzoates, *f* is essentially the same for a series of ethyl benzoates as *l*-menthyl benzoates. The value of *f* for a series of methyl esters is only approximately 20% less than that for a series of *i*-propyl esters.

Attacking Reagent.—For acid catalysis, *f* is practically the same for esterification as hydrolysis. For ortho-substituted benzoates, *f* also appears to be essentially the same for hydrolysis and esterification (base catalysis), that is, independent of attacking reagent OH^- or OCH_3^-.

Discussion.—The average median deviation of the substituent constants for the entire table is 0.08, the largest single median deviation is 0.28 for *A* of the substituent $(C_2H_5)_2CH$– (acid catalysis, acyl component). The average probable error of the reaction constants, *f*, for all of the reactions listed in Table II is 0.043, the largest probable

TABLE II

FREE ENERGY REACTION CONSTANTS, *f*, FOR ACID- AND BASE-CATALYZED ESTERIFICATION AND HYDROLYSIS OF *o*-SUBSTITUTED BENZOATES AND ALIPHATIC ESTERS

		n	*r*	Ref.
1, STRUCTURE VARIED IN ACYL COMPONENT				
a, Acid-catalyzed reactions				
Aliphatic series				
1, Hydrolysis of ethyl esters in 70% (vol.) aqueous acetone, 25°[b]	0.967 (1.00)	14	0.031	12–14
2, Esterification of carboxylic acids with methanol, 25°[b]	1.006 (1.00)	16	.025	7, 15
3, Esterification of carboxylic acids with ethanol, 25°[b]	1.005 (1.00)	18	.034	16
4, Hydrolysis of ethyl esters in 60% (vol.) aqueous acetone, 25°[b]	1.045 (1.00)	5	.009	17
5, Hydrolysis of methyl esters in water, 25°	0.98[a]	5	.044	18
Ortho-substituted benzoates				
6, Esterification of benzoic acids with methanol, 25°[b]	(1.000)	7	...	6a, b
7, Esterification of benzoic acids with cyclohexanol, 25°	0.735	7	.050	19
b, Base-catalyzed reactions				
Aliphatic series				
1, Hydrolysis of ethyl esters in 70% (vol.) aqueous acetone, 25°[b]	0.978 (1.00)	9	.018	13
2, Hydrolysis of ethyl esters in 85% (vol.) aqueous ethanol, 25°[b]	1.001 (1.00)	14	.020	20, 21
3, Hydrolysis of ethyl esters in 87.83% (wt.) aqueous ethanol, 30°	0.900	11	.017	11
4, Hydrolysis of benzyl esters in 60% (vol.) aqueous acetone, 25°[b]	1.005 (1.00)	7	.034	22
5, Hydrolysis of methyl esters in water, 25°	0.785	7	.036	23
6, Hydrolysis of ethyl esters in water, 25°	.833	7	.029	23
7, Hydrolysis of *n*-propyl esters in water, 25°	.863	7	.035	23
8, Hydrolysis of *i*-propyl esters in water, 25°	.972	7	.047	23
Ortho-substituted benzoates				
9, Hydrolysis of ethyl benzoates in 60% (vol.) aqueous acetone, 25°[b]	(1.000)	7	...	22
10, Hydrolysis of ethyl benzoates in 85% (vol.) aqueous ethanol, 25 and 30°	.978	5	.071	10, 11
11, Methanolysis of *l*-menthyl benzoates in methanol, 30°	.942	5	.042	8
2, STRUCTURE VARIED IN ALKYL COMPONENT				
a, Acid-catalyzed reactions				
Aliphatic series				
1, Hydrolysis of acetate esters in 60% (vol.) and 62% (wt.) aqueous acetone, 25°[b]	(1.000)	6	...	9a, 17, 24
2, Hydrolysis of acetate esters in water, 25°	0.64[a]	5	0.139	25
b, Base-catalyzed reactions				
Aliphatic series				
1, Hydrolysis of benzoate esters in 60% (vol.) aqueous acetone, 25°[b]	(1.000)	..	...	9b
2, Hydrolysis of acetate esters in 60% (vol.) and 62% (wt.) aqueous acetone, 25°	0.818	8	0.032	17, 24, 9b
3, Hydrolysis of formate esters in water, 25°	.394	5	.026	26
4, Hydrolysis of acetate esters in water, 25°	.820	8	.030	23, 25
5, Hydrolysis of propionate esters in water, 25°	.678	5	.054	23
6, Hydrolysis of *n*-butyrate esters in water, 25°	.697	5	.065	23
7, Hydrolysis of *i*-butyrate esters in water, 250	.977	5	.085	23
8, Hydrolysis of trimethylacetate esters in 16.67 % (vol.) dioxane–water, 25°	1.521	5	.049	23

[a] Too few substituents, and range in *A* values too small for this figure to be reliable. [b] A standard reaction series ($f \equiv 1$).

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(6) (a) R. J. Hartman and A. B. Gassman, THIS JOURNAL, **62**, 1559 (1940); (b) R. J. Hartman and A. M. Borders, *ibid.*, **59**, 2107 (1937).

(7) H. A. Smith and R. B. Hurley, *ibid.*, **72**, 112 (1950).

(8) R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, *ibid.*, **72**, 4511 (1950).

(9) (a) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938); (b) E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. **A57**, No. 13, 3 (1941); *ibid.*, No. 9, 3 (1941); *C. A.*, **38**, 6174 (1944).

(10) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937); and Ingold and Nathan, *ibid.*, 222 (1936).

(11) K. Kindler, see Hammett, (1), 191, ref. 3.

(12) H. A. Smith and R. R. Myers, THIS JOURNAL, **64**, 2362 (1942).

(13) G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940).

(14) V. C. Haskell and L. P. Hammett, THIS JOURNAL, **71**, 1284 (1949).

(15) H. A. Smith and J. Burn, *ibid.*, **66**, 1494 (1944); H. A. Smith, *ibid.*, **61**, 254 (1939).

(16) B. V. Bhide and J. J. Sudborough, *J. Ind. Inst. Sci.*, **8**, 89 (1925); *Chem. Centr.*, **97**, **I**, 80 (1926); see also J. J. Sudborough and L. L. Lloyd, *J. Chem. Soc.*, **75**, 467 (1899); J. J. Sudborough and M. K. Turner, *ibid.*, **101**, 237 (1912).

(17) W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936).

(18) A. Skrabal, *et al.*, *Monatsh.*, **45**, 148 (1924); **47**, 17, 30 (1926). **48**, 459 (1927); **50**, 369 (1928); M. H. Palomaa, *Ber.*, **71B**, 480 (1938); also see R. Korte and E. J. Salmi, *Suomen Kemistilehti*, **20B**, 8 (1947).

(19) R. J. Hartman, H. M. Hoogsteen and J. A. Moede, THIS JOURNAL, **66**, 1714 (1944).

(20) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1438 (1939).

(21) H. S. Levenson and H. A. Smith, THIS JOURNAL, **62**, 2324 (1940).

(22) E. Tommila, *Ann. Acad. Sci. Fennicae*, Ser. **A57**, No. 13, 3 (1941); *ibid.*, **A59**, No. 3, 3 (1942); *ibid.*, **A59**, No. 4, 3 (1942); *C. A.*, **38**, 6174 (1944).

(23) E. J. Salmi and R. Leimu, *Suomen Kemistilehti*, **20B**, 43 (1947); *C. A.*, **42**, 4031 (1948).

(24) P. N. Rylander and D. S. Tarbell, THIS JOURNAL, **72**, 3021 (1950).

(25) Reference 1, p. 211, footnote 73; p. 213.

(26) R. Leimu, R. Korte, E. Laaksonen and U. Lehmuskoski, *Suomen Kemistilehti*, **19B**, 93 (1946); *C. A.*, **41**, 5370 (1947).

error, 0.139, is for the acid-catalyzed hydrolysis of acetate esters in water at 25° (see footnote, Table II). Equation (1) covers variations in relative rate as large as approximately one millionfold. All comparisons of rates have been made at a temperature of 25° (or 30° in a few cases).

For ortho-substituted benzoates, Eq. (1) fails for the substituents H, F, NH_2 and OH. The former, H and F, follow the Hammett relationship,[27] that is, they show no ortho effect, while the latter, NH_2 and OH, probably show departure because of internal H bonding.[28]

Corresponding values of the substituent constant, A, for acid and base catalysis, listed in Table I, in most cases differ widely and bear no immediately obvious relationship to one another or to the English school theory of polarity of substituents.

The small effect of solvent on f indicates that the freezing out of solvent molecules in the formation of the transition state by bulky *o*-benzoate substituents or highly branched aliphatic groups in the acyl or alkyl component of an ester cannot be an important factor in determining relative rates for these reactions.

The much greater dependence of f values on structure in the acyl than the alkyl component may be the result of greater rigidity in the latter required by resonance in the carbalkoxy function.[29]

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[27] Reference 1, p. 206.

[28] G. E. K. Branch and D. L. Yabroff, THIS JOURNAL, **56**, 2568 (1934).

[29] See discussion by G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 69, 70.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Hydrogenation of Ethylene over Copper. I. Reproducing the Activity of the Catalyst

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One of the factors which determines the activity of a reduced copper catalyst toward the hydrogenation of ethylene is the amount of chemisorbed hydrogen on the catalyst surface. The kinetic experiments show that this hydrogen does not serve as a reactant. It thus can be considered to function as part of the catalyst. Three distinct methods of getting varying amounts of chemisorbed hydrogen of the surface are employed and the activity of the catalyst as a function of the parameter governing the amount of chemisorbed hydrogen on the surface is reported. Control of this coverage of chemisorbed hydrogen allows the activity to be reproduced to within 5% over a series of 50 runs.

Introduction

In recent years the technique of making evaporated metal films[2] has been adapted to the study of catalytically active films; indeed, this technique has largely replaced the older hydrogen-reduced catalysts of the type investigated here. Although this new method allows the preparation of generally more active and "cleaner" catalysts, it suffers from one unfortunate defect. The films so prepared cannot be restored to their original activity or put through any cycle that tests the reversibility of a loss in activity. For example, Beeck, Smith and Wheeler's nickel films, after each run on ethylene hydrogenation following the initial run, suffered small but progressive losses in activity which can be variously ascribed to impurities in the reactant gases, progressive poisoning of the surface by reactants or by-products, or loss of surface area by gumming or sintering.

We have reinvestigated the copper catalyst of Pease[3,4] for the hydrogenation of ethylene to ethane. The catalyst we have investigated, while never free of the hydrogen used in preparing it, can be returned at will to a standard activity by treatment with hydrogen. This ability to return to reference activity shows that the actual copper surface is not irreversibly altered. In the work reported here, the copper surface and the initial pressures of the reactant have been maintained unchanged.

Experimental

(a) Materials and Apparatus.—The catalyst was prepared by the reduction of 249.0 g. of Mallinckrodt CuO (wire form) with hydrogen at 130° for four days. The temperature was then raised gradually to 315° over a period of 3 hours; the temperature was lowered and held at 200° for 5 hours. The hydrogen outlet was then sealed off, and the catalyst was cooled slowly to room temperature with 1 atmosphere of hydrogen over it.

Circulation of reactant gases was unnecessary since the catalyst completely filled the bulb. The catalyst was protected from mercury vapor by Dry Ice traps inserted between the manometer and catalyst bulb. Poisoning by mercury is irreversible (Pease, ref. 3), and thus the ability to return to standard activity that emerges below is sufficient proof that the Dry Ice trap is adequate protection against mercury.

Electrolytic hydrogen was purified by passing it over platinized asbestos at 200° and freezing out the water formed with a Dry Ice trap followed by a liquid-nitrogen trap packed with glass wool. Mathieson C.P. grade ethylene was purified by condensation with liquid nitrogen, followed by alternate melting, freezing and pumping until air was apparently removed. As a final precaution the ethylene was passed through an activated-charcoal trap at −79°, condensed, and pumped off until it was all condensable. Mathieson helium was passed through an activated-charcoal trap in liquid nitrogen and stored with no other precaution. Absence of any poisoning effect showed this purification to be adequate.

The catalyst bulb was connected to the usual vacuum system. Pressure was measured on a mercury manometer equipped with a buzzer. A reading telescope was used to determine coincidence with the graduations of a mirrored scale to better than 0.1 mm.

The dead space of the reaction bulb was 100 cc. The

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[2] O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.* (*London*), **177**, 60 (1940).

[3] R. N. Pease, THIS JOURNAL, **45**, 1196 (1923).

[4] R. N. Pease and L. Stewart, *ibid.*, **47**, 1235 (1925).