TABLE III

NITRONAPHTHOIC ACIDS AND ESTERS[a]

Acid	M.p., °C.	Ester[b]	M.p., °C.
2-Nitro-1-naphthoic[3]	201–202 (202)[3]		
3-Nitro-1-naphthoic[41]	265.2–268.0 (270.5–271.5)[47]	Eth.	86.4–87.4 (87.5–88.5)[47]
4-Nitro-1-naphthoic[48]	224.1–224.5 (225–226)[47]	Meth.	109.2–110.3 (107.5–108.5)[47]
5-Nitro-1-naphthoic	239.2–240.9 (239)[49]	Meth.	107–108 (109–110)[49]
		Eth.	92.5–94 (92–93)[49]
6-Nitro-1-naphthoic[41]	224.9–225.3 (227–227.5)[47]	Eth.	108.9–109.9 (111.5–112)[47]
7-Nitro-1-naphthoic	261.0–263.5	Meth.	175.4–176.2
8 Nitro-1-naphthoic	215.2–217.2 (215)[49]		
1-Nitro-2-naphthoic	249.2–250.2 (239,[50] 246[51])	Meth.	146.6–147.3 (149–150)[52]
4-Nitro-2-naphthoic[53]	275–280 (270)[54]		
5-Nitro-2-naphthoic	294–295.5 (293)[55]	Eth.	108.6–109.3 (111)[55]
6-Nitro-2-naphthoic	323–325.5 (310)[40]	Eth.	181.1–182.3 (177)[40]
7-Nitro-2-naphthoic[39]	276–280 (262)[40]		
8-Nitro-2-naphthoic	292–293.5 (288)[55]	Eth.	120.5–121.1 (121)[55]
1-Naphthoic[c]	160.5–161.0 (160.5–162)[56]		
2-Naphthoic[c]	183.5–184.5 (184–185)[57]		
Benzoic[d]			

[a] All melting points are corrected. Values in parentheses are literature values. These were generally taken from those references which also describe the synthetic procedures that were followed. [b] Eth. = ethyl ester; Meth. = methyl ester. [c] A commercial sample (Distillation Products Ind.) was recrystallized twice from acetic acid, once from 95% ethanol and dried *in vacuo*. [d] The sample used in ref. 4 was used without further purification.

month interval, are: 3-nitro-1-naphthoic acid, 4.99, 5.02, 4.97, 5.00; and 8-nitro-2-naphthoic acid, 5.64, 5.63, 5.62. In the presence of 0.05 *N* lithium chloride, 5-nitro-, 6-nitro- and 7-nitro-1-naphthoic acid had values of 4.70, 4.92 and 5.12, or about 0.25 *pK* unit lower than in the absence of LiCl. Benzoic acid had *pK*'s in 0.05 *M* LiCl of 5.69 and 5.69, compared to the literature values of 5.65[4] and 5.66.[46]

Acknowledgment.—E. H. W. gratefully acknowledges an Eastman Kodak Fellowship, under which this work was completed. We also thank the Research Corporation for generous support.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Inductive Effects in Side Chain Reactions of Substituted Benzene Derivatives[1]

BY JOE L. ROBERTS AND H. H. JAFFÉ

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Statistical methods are used for the analysis of certain aspects of an empirical relation recently proposed by Taft and Lewis for the correlation of inductive effects.

Taft and Lewis have recently proposed a new empirical relation for separating inductive effects from resonance effects in side chain reactions of substituted benzene derivatives.[2] This relation is derived on the basis of the fundamental assumption that, within a given reaction series, the resonance effect of a substituent in the *m*-position is a constant fraction of the resonance effect of the same substituent in the *p*-position. The magnitude of this constant fraction is determined by the reaction series only and is the same for all substituents in any given series. Use of this relation between the resonance effect from the *m*- and *p*-position permits the elimination of these effects (*cf.* equation 3).

$$\log k_{\text{para}}/k^0 = \sigma_I\rho_I + R \quad (1)$$

$$\log k_{\text{meta}}/k^0 = \sigma_I\rho_I' + \alpha R \quad (2)$$

$$\log k_{\text{meta}}/k^0 = \alpha(\log k_{\text{para}}/k^0) - \sigma_I(\rho'_I - \alpha\rho_I) \quad (3)$$

where R is the resonance effect of a substituent in the *p*-position, σ_I is the Taft's inductive substituent constant, ρ_I and ρ_I' are inductive reaction constants and α is the constant relating *meta* and *para* resonance effects.

Taft and Lewis made the further simplifying assumption that the value of α derived from the alkaline hydrolysis of the ethyl benzoates, $\alpha = {}^1/_3$,

(1) This work was supported by the Office of Ordnance Research, U. S. Army.

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TABLE I

RESULTS OBTAINED BY THE USE OF EQUATIONS 3 AND 4

	Reaction	Ref.[a]	n[g]	From equation 3					From equation 4	
				α	$s\alpha$	ρ_I	r	s	ρ_I	
(1)	Ionization of benzoic acids, H_2O, 25°	1(a)	11	+0.220	0.148	+0.766	0.887	0.133	+0.675	0.688
(2)	Ionization of benzoic acids 50% aq. ethanol, 25°	1(l)[b]	8	+ .448	.072	+1.431	.992	.042	+1.575	.961
(3)	Alkaline sapn. of ethyl benzoates, 88% aq. ethanol, 30°	47(g)	8	+ .412	.041	+2.188	.997	.070	+2.394	.978
(4)	Alkaline sapn. of ethyl cinnamates, 88% aq. ethanol, 30°	55	8	+ .333	.028	+1.282	.998	.027	+1.29[c]	.994
(5)	Dissocn. of phenylboric acids, 25% aq. ethanol, 25°	13	5	+ .443	.032	+2.152	.999	.027	+2.168	.991
(6)	Solvolysis of benzoyl chloride in ethanol, 0°	65(a)[d]	8	+ .382	.053	+2.034	.997	.038	+2.005	.994
(7)	Ionization of phenols, H_2O, 25°	23(a)[e]	10	+ .425	.059	+2.446	.994	.053	+2.344	.983
(7')	Ionization of phenols, H_2O, 25°	23(a)[f]	6	+ .077	.083	+2.281	.997	.074	.....	...
(8)	Ionization of anilinium ions, H_2O, 25°	26(a)[e]	7	+ .277	.066	+2.934	.991	.097	+2.949	.997
(8')	Ionization of anilinium ions, H_2O, 25°	26(a)[f]	4	− .041	.608	+2.921	.995	.168	.....	...
(9)	Reacn. of benzoic acids with diphenyldiazomethane in ethanol, 30°	43	5	+ .553	.078	+ .962	.999	.015	+1.029	.992

[a] Reaction number in ref. 5. [b] The data for the substituent $Si(CH_3)_3$ deviated seriously from equations 3 and 4 and were not used for these calculations. [c] The results for equation 4 are from ref. 2, Table I. [d] Data for the substituent OCH_3 were excluded; see ref. 2, Table I, footnote 6. [e] Only those substituents for which Taft and Lewis used $\alpha = {}^1/_3$ were used for these calculations. [f] Only those substituents for which Taft and Lewis used $\alpha = {}^1/_{10}$ were used for these calculations. [g] Number of substituents for which data are available.

is applicable to all reaction series, and obtained equation 4. They applied this equation to a

$$\log (k_{\text{meta}}/k^\circ) - {}^1/_3 \log (k_{\text{para}}/k^\circ) = \sigma_I(\rho_I' - {}^1/_3\rho_I) \quad (4)$$

limited number of reaction series and found that the left-hand side was quite well correlated with σ_I-values.

We have now undertaken a more exhaustive study of equation 3, with particular emphasis on the value of α. We have extracted from our files all those reaction series for which rate or equilibrium data were available for at least four substituents in both the *m*- and *p*-positions. Using standard least squares methods,[3] we have fitted the data to equations 3 and 4 and have evaluated the improvement due to the variation of α by an analysis of the variance.[4] We have also evaluated best estimates of α and of the quantity $(\rho_I' - \alpha\rho_I)$ from eq. 4 and of $(\rho_I' - {}^1/_3\, \rho_I)$ from eq. 3. Assuming $\rho_I' = \rho_I$, we have then estimated a value of ρ_I for both equations. Some of the results obtained by fitting data to both equation 3 and equation 4 are compared in Table I.

TABLE II

ANALYSIS OF VARIANCE

Source	Degrees of freedom	Sum of squares	Mean squares	F[a]
Linear regression (eq. 4)	1	36.958	36.958	9910**
Additional due to multiple regression (eq. 3)	1	0.708	0.708	190**
Deviation from M.R.	242	0.904	0.00373	
Total	244	38.570		

[a] A double asterisk indicates significance at the 99% level.

Taft and Lewis have shown that reaction series do not follow eq. 3 or 4 in their simple form whenever considerable changes in resonance between initial and transition (or final) states occur. Such series require the use of σ^+- or σ^--values in the application of the Hammett equation; they were excluded from the analysis of variance calculations. Further, free radical reactions were also excluded, and will be discussed separately below.

The results of the analysis of variance of 43 reaction series are given in Table II. It is seen that permitting α to be an adjustable parameter leads to a considerable and *highly significant* improvement of the fit. However, the portion of the total variance accounted for by the linear regression (equation 4) is so overwhelming that we concur with Taft and Lewis that their assumption of $\alpha = {}^1/_3$ is a highly useful one. Further, the uncertainties in the α-values obtained by the multiple regression procedure are very large, probably both because of the relative scarcity of data and the accumulation of experimental error. Each point in the linear plots of equation 3 necessarily involves three pieces of data, and each of these is subject to experimental uncertainty. The range of α-values obtained and the range of the corresponding uncertainties are shown in Table III. In view of the large uncertainties, individual values are not reported with the exception of the examples shown in Table I. It is seen from Table III that the standard deviations of α (s_α) are such that the observed differences cannot in any particular case be shown to be significant, although the significance of the improvement of fit due to the multiple regression clearly demonstrates that there are significant differences, at least between some of the α's.[4] There is no apparent relation between the magnitudes of α and its standard deviation.

Taft and Lewis have proposed that different α-values should be employed for conjugating (${}^1/_{10}$) and non-conjugating substituents (${}^1/_3$) in reaction series involving a major change in conjugation

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(3) G. W. Snedecor, "Statistical Methods," 4th edition, Iowa State College Press, Ames, Iowa. Chapts. VI, XIII.

(4) H. H. Jaffé, *J. Org. Chem.*, **23**, 874 (1958).

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(6) J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2167 (1953).

TABLE III[a]

THE DISTRIBUTION OF α AND s_α

s_α \ α	(−1.0 to −0.5)	(−0.5 to 0)	(0 to 0.1)	(0.1 to 0.2)	(0.2 to 0.3)	(0.3 to 0.4)	(0.4 to 0.5)	(0.5 to 1.0)	Total
<5% of α					2	1		2	5
5–10%				1		3	3	1	8
10–20%					2	1	1		4
20–30%	1				1	2	1	1	6
30–50%	1			1	1		2	2	7
>50%		6	1	1	3	1	1		13
Total	2	6	1	3	9	8	8	6	43

[a] The numbers in the table are the numbers of reactions for which the parameters lie between the limits given in the column and row headings.

between substituent and reacting center. No attempt has been made to treat two such values as adjustable parameters since the experimental material available is too limited and the uncertainties in α-values would be even larger than for the two parameter equation. However, for two such reactions we divided the data into two groups, one containing conjugating substituents only, the other containing non-conjugating substituents only. We then separately fitted each of these two groups to equation 3. The results are given in Table I, reactions 7, 7′, 8 and 8′.

The one parameter equation 4 is found to fit the experimental data with surprising precision. Table IV lists a frequency distribution of the correlation coefficients for reaction series, and it is seen that the precision greatly surpasses that of the standard Hammett equation.[5]

TABLE IV[a]

THE DISTRIBUTION OF s_I AND r

r \ s_I	0 to 0.2	0.2 to 0.5	0.5 to 1.0	1.0 to 2.0	2.0 to 5.0	Total
>0.99		1	2	2	2	7
0.95–0.99			1	5	6	12
.90– .95			3	1	2	6
.80– .90			5	2	1	8
.50– .80	3	1	1			5
<0.50	5					5
Total	8	2	12	10	11	43

[a] The numbers in the table are the numbers of reactions for which the parameters lie between the limits given in the column and row headings.

It appears reasonable that the ρ'-values of Roberts and Moreland[6] for the [2,2,2]bicyclooctane derivatives should be correlated with the ρ_I-values given in this paper for the corresponding aromatic series, since both sets of values reflect transmission of inductive effects through spacially similar systems. The ρ'-and ρ_I-values are compared in Table V. The anticipated constancy of the ratio, ρ_I/ρ', appears to be borne out, although it should be noted that the value for the diphenyldiazomethane reaction is somewhat higher than the value for the other two reactions.[7] It is interesting to note that Roberts and Moreland obtained equivalent results for the diphenyldiazomethane reaction in comparing ρ' to Hammett ρ-values. Additional information about the application of equations 3 and 4 to these reactions is contained in Table I.

TABLE V

COMPARISON OF ρ_I- AND ρ'-VALUES

Reaction	ρ_I[a]	ρ_I[b]	ρ'	ρ_I[a]/ρ'	Ref.[c]
Ionization of carboxylic acids, 50% aq. EtOH, 25°	+1.431	+1.575	+1.464	0.98	1(e)
Alkaline hydrol. of ethyl esters, 88% aq. EtOH, 30°	+2.188	+2.394	+2.24	0.98	47(g)
Reacn. of carboxylic acids and diphenyldiazomethane in ethanol, 30°	+0.962	+1.029	+0.698	1.38	43

[a] ρ_I obtained from eq. 3. [b] ρ_I obtained from eq. 4. [c] Reaction number in ref. 5.

TABLE VIa[a]

THE DISTRIBUTION OF ρ_I AND r FOR FREE RADICAL REACTIONS

r \ ρ_I	(0 to 0.2)	(0.2 to 0.5)	(0.9 to 1.4)	Total
>0.99	1	3	1	5
0.95–0.99		1	2	3
.90– .95	1		1	2
.50– .80		2		2
<0.50	1			1
Total	3	6	4	13

[a] The numbers in the table are the numbers of reactions for which the parameters lie between the limits given in the column and row headings.

TABLE VIb[a]

THE DISTRIBUTION OF α AND s_α FOR FREE RADICAL REACTIONS

$s(\alpha)$ \ α	(−0.2 to 0)	(0 to 0.5)	(0.5 to 0.8)	(1.0 to 2.0)	Total
<5% of α			1		1
5–10%			3		3
10–20%				1	1
30–50%		1		1	2
50–100%	1		1		2
>100%	2	1	1		4
Total	3	2	6	2	13

[a] The numbers in the table are the numbers of reactions for which the parameters lie between the limits given in the column and row headings.

Finally it appeared of interest to examine the application of equation 3 to reaction series known to proceed *via* a free radical mechanism. The pertinent data for a group of such reaction series are summarized in Table VI. Equation 3 appears to apply to these reaction series, although the precision is somewhat lower than for polar reactions; this may well be due to the larger experimental errors usually inherent in the measurement of the rates of free radical reactions. However, the most notable feature of Table VI is the relatively large magnitude of the α-values. Whether these large values occur because resonance effects of *p*-substituents are relatively less important, or those of *m*-substituents more important is difficult to decide at this time.

Acknowledgment.—The authors are grateful to Professor Robert W. Taft, Jr., for valuable dis-

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(7) Professor Taft, in a private communication, has offered the following comment concerning the diphenyldiazomethane reaction. 'The diphenyldiazomethane reactivities are actually a composite of two, one going to the ester and the other to the ether. Perhaps a change in the relative importance of these two reactions accounts for the apparent anomaly."

cussions during the course of this work. They are also grateful to the Avco Manufacturing Corp., which kindly made time available on an IBM 650 MDDPM to perform the statistical analyses.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA STATE UNIVERSITY]

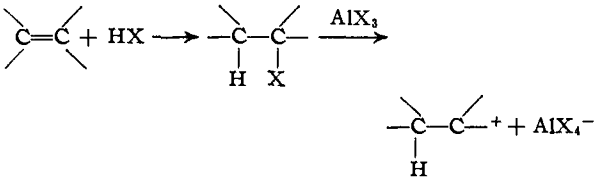
Kinetics of the Friedel–Crafts Ethylation of Benzene with Ethylene and with Ethylene-C^{14}

BY ERNEST M. HODNETT AND CHARLES F. FELDMAN, JR.[1]

RECEIVED AUGUST 8, 1958

A tenfold excess of benzene was alkylated with ethylene and aluminum bromide in a constant-volume recycle system. The over-all rate expression was found to be $-d[C_2H_4]/dt = k_2[C_2H_4][AlBr_3]$. When ethylene-$C^{14}$ was used, no change in specific radioactivity occurred during the reaction, indicating that the reaction of ethylene is fast and non-rate-determining.

Although the alkylation of benzene with ethylene has been known[2] since 1879 and has been used industrially for some years, the reaction mechanism has not been elucidated clearly. Kinetic data are sparse and not always reliable for this reaction, as for Friedel–Crafts alkylations in general. The reaction has been the subject of many reviews.[3] Thomas proposed a mechanism that involves the action of hydrogen chloride and aluminum chloride to form chloroaluminic acid, and the subsequent ionization of this acid. The proton so produced can attack any carbon–carbon double bond forming a carbonium ion which reacts further. However, Ulrich, Keutman and Geierhaus[4] presented evidence for the formation of an alkyl halide from the olefin and hydrogen halide, and its subsequent ionization by aluminum chloride to a carbonium ion. This mechanism indicates a similarity between Friedel–Crafts alkylations with olefins and those with alkyl halides.



In order to understand the mechanism of alkylation of benzene with olefins, it is necessary to know: (1) the nature of the catalyst–olefin complex, (2) the contribution of a carbonium-ion process, and (3) the contribution of a displacement process. The kinetics of the ethylation of benzene using ethylene and ethylene-C^{14} under the catalytic influence of aluminum bromide have been determined in this investigation as a step toward a better understanding of the reaction.

Results and Discussion

The Reaction of Ethylene with Benzene.—The monoalkylation of benzene with ethylene using aluminum bromide as a catalyst was studied kinetically at approximately 100:10:1 ratios of benzene : ethylene : aluminum bromide. The excess benzene was used to make the reaction rate independent of its concentration and to minimize dialkylation. The reaction was homogeneous at the start, but became heterogeneous as a Friedel–Crafts oil was formed. When the data are plotted as ethylene pressure *versus* time, the curves are similar to those obtained by Jungk, Smoot and Brown[5] in alkylations of benzene with ethyl bromide using aluminum bromide as the catalyst.

The aluminum bromide catalyst was freshly distilled prior to each run and treated carefully to give as pure a catalyst as possible. However, the relative catalytic activity of the aluminum bromide from one run to another was not as constant as desired.

The reaction rates were followed by the uptake of ethylene at constant volume. Changing the rate of flow of ethylene through the reaction mixture had no effect on the reaction rate. Changes in the initial concentration of aluminum bromide resulted in changes of the specific rate constant k_1. When the first-order rate constants, k_1, are divided by the initial concentrations of the aluminum bromide, a second-order constant, k_2, is obtained which is fairly constant over the range of aluminum bromide concentrations used. The data for four runs are summarized in Table I.

The kinetic data for the first part of each run show a first-order dependence on ethylene pressure

$$-d[C_2H_4]/dt = k_1[C_2H_4]$$

However, since the rate constant, k_1, varies linearly also with the initial concentration of aluminum bromide, the rate expression must have the concentrations of both components to the first power.

$$-d[C_2H_4]/dt = k_2[C_2H_4][AlBr_3]$$

The tenfold excess of benzene in each case did not permit its detection in the rate expression.

The Alkylation of Benzene with Ethylene-C^{14}.—A kinetic isotope effect can be demonstrated by observing the change in the isotopic concentration

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