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The ρ - ρ Relation and Transmission of Electronic Effects in the Reaction of Phenylacetic Acids with Diphenyldiazomethane¹

BY RORY MORE O'FERRALL AND SIDNEY I. MILLER

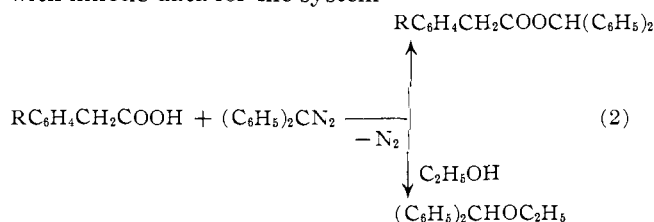
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Rate data for the reactions of thirteen substituted phenylacetic acids (*p*-NH₂, *p*-CH₃, *p*-CH₃O, H, *m*-CH₃O, *m*-NO₂, *p*-Cl, *p*-Br, *p*-I, *m*-Cl, *m*-I, *m*-Br, *p*-NO₂) with diphenyldiazomethane (DDM) in ethanol have been obtained. The range of the activation parameters for ΔH^\ddagger is 13.8 to 15.0 kcal. mole⁻¹ and for ΔS^\ddagger -8 to -12 cal. deg.⁻¹ mole⁻¹. Satisfactory Hammett lines have been calculated: at 26.05°, $\log k = 0.34\sigma - 0.0538$; at 35.6°, $\log k = 0.37\sigma + 0.2523$. A derivation of a ρ - ρ' relation, $\rho/\rho' = \text{constant}$, has been given and a test of its validity has been initiated. The systems of interest are the pK's of acids, R-G-COOH, which yield ρ 's and the rate constants of these acids in the DDM reaction which yield ρ 's. For the solvent ethanol $\rho/\rho' \approx 2.0$; this may be taken as a measure of the effectiveness with which the electronic demands of the site of the DDM reaction are relayed to the substituent.

Considerable effort has gone into the dissection of the Hammett equation^{2,3}

$$\log k = \rho\sigma + \text{constant} \quad (1)$$

Substituent constants σ have proliferated and various viewpoints on their use have been expressed. ρ , which characterizes the reaction, the reaction conditions, and the ease of transmission of electronic effects from the substituent to the reaction center, has attracted somewhat less attention. In this paper we launch a phenomenological inquiry into the basis of ρ of eq. 1. A ρ - ρ relation is derived and it is then tested with kinetic data for the system



The ρ - ρ Relation.—Certain interpretations of ρ are inherent in the formalism of linear correlations. Previously it was shown that for

$$\log k = f(\sigma, x_1, x_2, x_3 \dots) \quad (3)$$

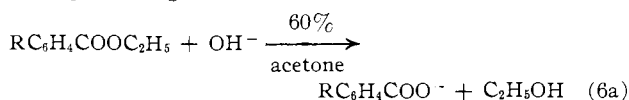
in which $\log k$ is separately linear in each of the structural or environmental factors σ , $x_1 = \sigma^+$, $x_2 = 1/T$, etc.; it followed rigorously for each x that

$$\log k = a + b_1\sigma + b_2x + q\sigma x \quad (4)$$

and

$$\Delta\rho/\Delta x = q \quad (5)$$

where a , b_1 , b_2 , and q are parameters.⁴ To illustrate how the several factors governing ρ can be treated, two examples are given. For the reaction⁵



89 rate constants in l. mole⁻¹ sec.⁻¹ in the temperature range $T = 273$ – 313°K . are contained in

$$\log k = 8.145 + 0.3022\sigma + 319.1/T + 587.3\sigma/T \quad (6b)$$

which by eq. 5 yields

$$\Delta\rho = 587.3 \Delta(1/T) \quad (6c)$$

For the dissociations at 25°⁶

(1) Supported by the U. S. Army Research Office (Durham).

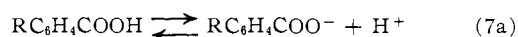
(2) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(3) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

(4) (a) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959); (b) G. S. Krishnamurthy and S. I. Miller, *ibid.*, **83**, 3961 (1961).

(5) Data are taken from ref. 2, reactions 47h–47k of Table 2. The method of calculation is given in ref. 4b.

(6) J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454, 466, 472 (1941); M. Kilpatrick and R. D. Eanes, *J. Am. Chem. Soc.*, **65**, 589 (1943). For eq. 7b the variance = 0.0146 and the confidence levels of the coefficients are 99, 90, and 97%, respectively, as given by Students' *t*.^{4b}



67 K_i 's were measured in the range of dielectric constant 24–78.5 D.

$$\log K_i/K_H = 0.9019 + 1.037\sigma - 2.602/D + 9.127\sigma/D \quad (7b)$$

and

$$\Delta\rho = 9.127 \Delta(1/D) \quad (7c)$$

In the same way, the dependence of ρ on other factors x may be displayed.

Hammett⁷ and Jaffé^{2,8} independently noted that for pairs of processes, e.g., acid dissociation and ester saponification

$$\rho_{\text{ArT}_1\text{COOH}}/\rho_{\text{ArT}_1\text{COOC}_2\text{H}_5} = \rho_{\text{ArT}_2\text{COOH}}/\rho_{\text{ArT}_2\text{COOC}_2\text{H}_5} = \pi \quad (8)$$

Jaffé rationalized eq. 8 on theoretical grounds and provided most of the published examples of its use.⁸ Several groups have made comparisons of the type^{9–11}

$$\rho_{\text{R-G-COOH}}/\rho_{\text{ArCOOH}} = \rho_{\text{R-G-COOC}_2\text{H}_5}/\rho_{\text{ArCOOC}_2\text{H}_5} = \dots \quad (9)$$

Typical series of compounds, ArT_i– or RG–, are given in Table I. It is worth noting that eq. 8 emphasizes the electronic demands of the reaction site as compared to the parent family of acids while eq. 9 compares the effectiveness of transmittal of electronic effects through any group G with that of similar benzoic acid derivatives.

The assumptions or requirements that eq. 8 be valid are instructive and can be made explicit from the analysis of a multiple variation as in eq. 4 and 5. Now suppose that the factors which determine ρ can be lumped together in an independent variable termed s . Then $\log k = f(\sigma, s)$ and, subject to the condition that $\log k$ is separately linear in σ or s

$$\Delta\rho/\Delta s = q \quad (10)$$

for a given reaction, e.g., the pK's of acids ArT_iCOOH. For another reaction, e.g., the hydrolysis of esters, ArT_iCOOC₂H₅

$$\Delta\rho'/\Delta s = q' \quad (11a)$$

Therefore

$$(\rho - \rho_0)/(\rho' - \rho'_0) = q/q' \quad (11b)$$

in which ρ_0 and ρ'_0 stem from the reactions of ArT₀COOH and ArT₀COOC₂H₅, respectively. The reduction of 11b to eq. 8, $\rho/\rho' = \pi$, is simple. There are many series in which the substituent is completely insulated or just too far away from the reaction site to be sensitive to its demands. Here the interposed group is T₀ and $\rho_0 = \rho'_0 = 0$. Other approaches to this reduction will be given elsewhere.¹²

(7) L. P. Hammett, in lecture notes taken by S. I. M. at Columbia University, 1948–1949.

(8) (a) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953); (b) S. Yeh and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 3287 (1959).

(9) E. Imoto, et al., *Nippon Kagaku Zasshi*, **80**, 1021, 1024, 1293, 1297, 1300, 1307 (1959).

(10) M. Charton, *J. Org. Chem.*, **26**, 735 (1961).

(11) R. E. Dessy and J. Kim, *J. Am. Chem. Soc.*, **83**, 1167 (1961)

(12) J. D. S. Ritter and S. I. Miller, to be published.

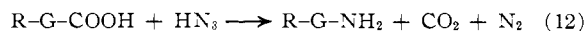
TABLE I
 HAMMETT ρ -VALUES FOR REACTIONS OF ACIDS OR THEIR DERIVATIVES^a

R-G-COOH	pK, H ₂ O 25°	pK, 50% C ₂ H ₅ OH, 25°	R-G-COOC ₂ H ₅ + OH- 88% C ₂ H ₅ OH, 30°	R-G-COOH + DDM, C ₂ H ₅ OH, 30°
1 ArCOOH	1.00	1.4-1.6	2.431	0.940
2 ArCH ₂ COOH	0.519 ^b		0.824	0.35 ^c
3 ArCH ₂ CH ₂ COOH	.212 ^d	0.344 ^d	0.59 ^d	
4 <i>trans</i> -ArCH=CHCOOH	.466		1.32 ^d	
5 <i>cis</i> -ArCH=CHCOOH	.643 ^d		1.122 ^d	
6 ArCH=CHCOCO ₂ H	-.054		1.329	
7 <i>p</i> -Ar-C ₆ H ₄ COOH	(.34) ^h	(.48) ⁱ	0.608	
8 <i>trans</i> -ArCH(CH ₂)CHCOOH	.182 ^e	.473 ^d	0.812 ^d	
9 <i>cis</i> -ArCH(CH ₂)CHCOOH	(.32) ^h	.436	1.014 ^d	
10 ArC≡CCOOH	(.34) ^h	.48 ^f	1.1 ⁿ	0.31 ^f
11 5-Furanyl-COOH	1.396 ^g		2.973 ^g	
12 5-Thienyl-COOH	1.076 ^g		2.437 ^g	
13 R-(2-CH ₃ C ₆ H ₃)-COOH	1.28 ⁱ	1.673 ^k	2.1 ⁱ	0.946
14 R-(2,6-(CH ₃) ₂ C ₆ H ₂)-COOH		1.4 ^k		0.69 ^k
15 ArOCH ₂ COOH	0.3 ^l		1.1 ^m	

^a ρ -Value from ref. 2, unless otherwise noted. ^b Ref. 25. ^c This study. ^d Ref. 29. ^e E. N. Trachtenburg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958). ^f Ref. 28. ^g Ref. 9. ^h Estimated in Fig. 1 or 2. ⁱ Ref. 30. ^j Estimated from data in ref. 2. ^k Ref. 17. ^l N. V. Hayes and G. E. K. Branch, *J. Am. Chem. Soc.*, **65**, 1555 (1943). ^m R. F. Brown and H. C. Newsom, *J. Org. Chem.*, **27**, 3010 (1962): ρ -value at 0°. ⁿ Ref. 14.

The preceding derivation appears to be valuable theoretically and eq. 8 may be useful empirically. Examples of the type eq. 6c and 7c should be illustrative of two s -factors.⁴ However, the ultimate question as to the nature of this factor s as it relates to Ar-T- must be deferred. First, what is the experimental basis of eq. 8 and does it have utility? We believe that both the successes and the failures in the experimental tests of eq. 8 will furnish important information on which a fundamental approach to s must be based. This is our present emphasis.

Despite all of the work relating reactivity to structure, rate data taken under uniform conditions for a test of eq. 8 are scarce. Table I and Fig. 1 and 2 show ρ - ρ data for acids and their derivatives R-G-COS. In the figures, the abscissa consists of ρ 's for the dissociations of acids R-G-COOH in water at 25°; the ordinate consists of ρ 's for any other reaction, e.g., the basic hydrolysis of the esters R-G-COOC₂H₅ in 88% ethanol at 30°. This is line A, Fig. 1. Based on one or two reported ρ 's, it is of course possible to sketch in many lines and thus attempt to predict many more ρ 's. Line C, Fig. 2, is the beginning of a ρ - ρ relation involving the pK's of the acids R-G-COOH in 50% ethanol at 25°. Line D, Fig. 2, based only on data for ArCOOH, is a potential or predicted ρ - ρ relation for the reactions¹³



Line B, Fig. 1, is the subject of the present study and will be discussed later.

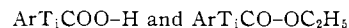
It thus appears that the hydrolysis reaction, line A, Fig. 1, provides the only satisfactory test of eq. 8. As indicated earlier this line has been constrained to pass through the origin. For points 7, 9, and 10 the abscissa had to be estimated. Otherwise, the data stem from many sources and it may be necessary to repeat some of the work.¹⁴ Excluding point 6 for the benzylidene-pyruvoyl group, the median deviation in ρ along the abscissa is ± 0.1 and along the ordinate ± 0.2 . This is

(13) L. H. Briggs and J. W. Littleton, *J. Chem. Soc.*, 421 (1943).

(14) For example, ρ for the hydrolysis of the ethyl phenylpropiolates has been remeasured. Professor F. Fuchs (private communication) finds $\rho = 1.1$ as compared to the older value of $\rho = 1.9$.¹⁵

(15) J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955).

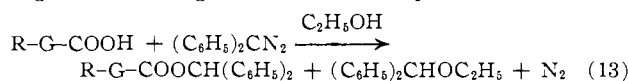
only slightly larger than that found by Jaffé in his survey of many ρ 's.² Of course, acid dissociation and ester hydrolysis involve the relay of electronic effects to two different reaction sites



In fact, the hydrolysis reaction involves one or more intermediates which may go on to form products or revert to reactants.¹⁶ Although the over-all rate constants are composite, they did not lead to a complex or composite ρ , at least in the hydrolyses of the methyl benzoates¹⁶: there is no assurance, however, that this will remain true for all of the families of esters of Table I. Despite all of these potential sources of deviation from eq. 8, the correlation given by line A, Fig. 1, is moderately encouraging and $\rho/\rho' = 2.4 \pm 0.2$ for line A.

Results

The kinetics and mechanism of the reaction of the acids with diphenyldiazomethane (DDM) are reasonably well understood.^{17,18} This reaction has the advantage of involving the transfer of a proton from the car-



boxylate to the α -carbon atom of the DDM in the rate-determining step. Subsequent to this slow transfer, there appears to be a partitioning into paths leading either to ester or ethyl benzhydryl ether.^{18a} One may suppose, therefore, that in the transition state there is partial breaking of the O-H bond of the acid and that the factors involved here will be closely related to those that determine the pK of the acid. Conditions of temperature and environment being similar, this would seem to provide an especially simple case for an initial test of eq. 8.

Rate data for eq. 2 are given in Table II. Although we were satisfied with the precision of our rate con-

(16) M. L. Bender and R. J. Thomas, *ibid.*, **83**, 4189 (1961).

(17) J. D. Roberts and C. M. Regan, *ibid.*, **76**, 939 (1954); J. D. Roberts and J. A. Yancey, *ibid.*, **73**, 1011 (1951).

(18) (a) J. D. Roberts, W. Watanabe, and R. E. McMahon, *ibid.*, **73**, 760 (1951); (b) J. D. Roberts and C. M. Regan, *ibid.*, **74**, 3695 (1952); (c) J. D. Roberts and W. Watanabe, *ibid.*, **72**, 4869 (1950).

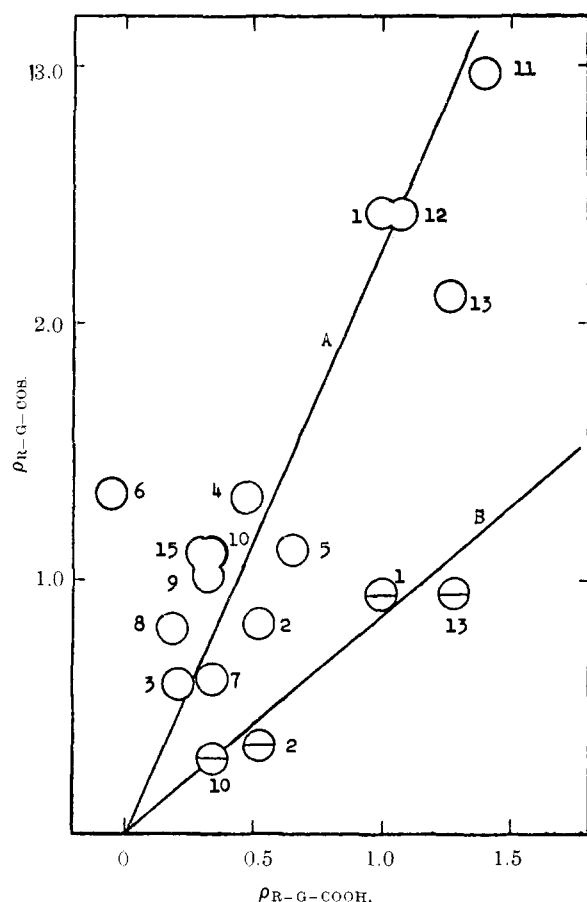


Fig. 1.— ρ - ρ relation: ρ_{R-G-CO_2H} for reactions of acids or their derivatives vs. $\rho_{R-G-COOH}$ for the pK 's in water at 25°: A, upper curve, the basic hydrolysis of $R-G-COOC_2H_5$ in 88% ethanol at 30°; B, lower curve, the reaction of $R-G-COOH$ with DDM in ethanol at 30°; numbers refer to the acids in Table I.

stants, it is fair to point out that there are often unexplained discrepancies of the order of 10–20% in the rate constants of the reaction of benzoic acid with DDM as published by different groups (see Experimental for details). For a wide range of phenylacetic acids, the rate constant changes by a factor of *ca.* 2. This of course leads to a narrow spectrum of activation parameters.

Rate data for the phenylacetic acid series are particularly interesting in their relation to the effects of substituents on reactivity.^{19–22} Because of the insulating effect of the methylene group, such data have been used to estimate the inductive effect of a given substituent. Carried over to other series in which conjugation is possible, this inductive effect can be subtracted from the total effect of the substituent to give a measure of its resonance effect.^{20,21} With this in mind, we correlated our rate data with several types of substituent factors (Table III). Clearly, whether one uses "standard" σ 's based on the pK 's of benzoic acids,²³ σ^m 's based on selected benzoic acids in which mesomeric interactions are presumed to be minimal,²⁴ or the pK 's of the phenylacetic acids,²⁵ good correlations are ob-

(19) F. H. Westheimer, *J. Am. Chem. Soc.*, **61**, 1977 (1939).

(20) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice Hall, Inc., New York, N. Y., 1941, Ch. VI.

(21) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960), and related work.

(22) R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *J. Chem. Soc.*, 3247 (1961).

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

(24) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(25) A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, 1093 (1961).

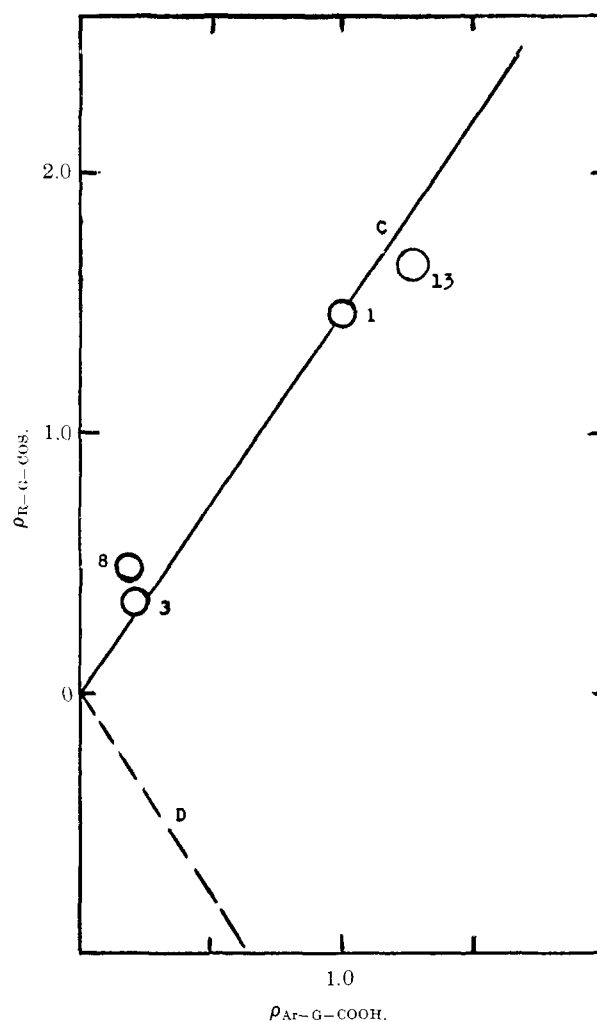


Fig. 2.— ρ - ρ relation: ρ_{R-G-CO_2H} for the reactions of acids or their derivatives vs. $\rho_{R-G-COOH}$ for the pK 's in water at 25°: C, the pK 's of $R-G-COOH$ in 50% ethanol at 25°; D, a predicted line, say for reaction 12, ref. 13; numbers refer to the acids in Table I.

tained. In contrast, Taft's inductive constants σ^* , deriving from inductive effects in aliphatic compounds,²⁶ gave a distinctly poorer correlation. These results reinforce the view that polar effects of R, even in two insulated systems $RC_6H_4CH_2COOH$ and RCH_2COOH , are different.²¹ That the polar effect of R was intimately related to its immediate structural environment has long been evident—albeit in a different context—from the differences in alkyl-R and aryl-R dipole moments.²⁷

It is worth pointing out that several workers have analyzed the data for reactions in which conjugation between the reaction site and the aryl nucleus is precluded. For the pK 's of phenylacetic acids, satisfactory correlations have been obtained with σ^n .^{24,25} Making use of data for several insulated systems, Taft has devised a new scale, σ^0 , which differs significantly from the σ^n scale at the strongly electron-releasing end with more negative σ 's, *e.g.*, $\sigma^0 = -0.38$ vs. $\sigma^n = -0.17$ for the *p*-amino substituent. Making use of much the same data, Norman, *et al.*, have proposed still another scale, σ_G , which differs significantly from the others on the electron-withdrawing side with diminished σ 's for the nitro and acyl substituents.²² While our DDM rate data give satisfactory correlations either

(26) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

(27) Reference 20, p. 146.

TABLE II
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
REACTION

$$\text{RC}_6\text{H}_4\text{CH}_2\text{COOH} + (\text{C}_6\text{H}_5)_2\text{CN}_2 \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{RC}_6\text{H}_4\text{CH}_2\text{COOCH}(\text{C}_6\text{H}_5)_2 + \text{C}_2\text{H}_5\text{OCH}(\text{C}_6\text{H}_5)_2 + \text{N}_2$$

Substituent	k , l. mole ⁻¹ min. ⁻¹	ΔH^\ddagger , kcal. mole ⁻¹	ΔS^\ddagger , cal. deg. ⁻¹ mole ⁻¹
R	(26.05 ± 0.1) ^o (35.6 ± 0.1) ^o		
<i>p</i> -NH ₂	1.40		
<i>p</i> -CH ₃	0.76		
<i>p</i> -CH ₃ O	.75	1.63	14.3
H	.81	1.82 ^d	15.0
<i>m</i> -CH ₃ O	.90 ^f	1.93	14.1
<i>p</i> -Cl	1.05	2.29	14.4
<i>p</i> -Br	1.08		
<i>p</i> -I	1.10	2.39	14.3
<i>m</i> -Cl	1.17	2.55	14.4
<i>m</i> -I	1.25	2.64	13.8
<i>m</i> -Br	1.20		
<i>p</i> -NO ₂	1.53 ^f	3.43 ^e	14.9
<i>m</i> -NO ₂	1.59		

^o Uncertainty in k_2 : ±3%, normally three runs. ^b Uncertainty < ±1 kcal. mole⁻¹. ^c Uncertainty: ±1.0 cal. deg.⁻¹ mole⁻¹. ^d Five runs. ^e Seven runs. ^f Four runs.

TABLE III

HAMMETT-TYPE CORRELATIONS FOR THE REACTION OF DIPHENYLDIAZOMETHANE WITH THE PHENYLACETIC ACIDS IN ETHANOL

Temp., °C.	Substituent factor	ρ	$\log k_0^a$	r^b	s^c	n^d
26	σ^{23}	0.339	-0.0538	0.977	0.0058	12
26	σ^{n24}	.373	-.0721	.988	.0032	11
26	σ^{*26}	.447	-.1319	.890	.0267	12
26	pK^{25}	.754	4.176	.978	.0052	12
36	σ^{23}	.362	0.2718	.967	.0074	9
36	σ^{n24}	.401	0.2523	.985	.0033	9

^a Intercept of eq. 1. ^b Correlation coefficient. ^c Standard deviation. ^d Number of compounds used in correlation.

with σ^0 's or σ_C 's yielding slightly different ρ 's, a change to these σ 's does not appear to be warranted at this time.

For use in the ρ - ρ relation, eq. 8, we used $\rho = 0.35$ interpolated to 30° from the "standard" σ -correlation of Table III. Moreover, the ρ 's of Table I are generally based on "standard" σ 's. Now it is possible to vary ρ somewhat by using different σ -scales. But such a variation is within the uncertainty of the ρ - ρ relation and is not important in this application. This ρ -value can be compared with $\rho = 0.94$ for the DDM reactions of the benzoic acids. The effect of a $-\text{CH}_2-$ group in reducing the transmission of electronic effects to a reaction center by a factor of ca. 2.7 is well established.^{20,21}

The present study of the phenylacetic acid-DDM reaction contributes point 2 (line B, Fig. 1). Together with the benzoic acids (point 1), a working ρ - ρ relation is established. Because ρ for the pK 's of the phenylpropionic acids was known only for 50% ethanol,^{28,29} line C (Fig. 2) was used to estimate the ρ -value for water at 25° so that its position at 10 on line B, Fig. 1, is an estimate.

We can also compare corresponding ρ -values for the pK 's of the acids with ρ 's for their reactions with DDM in the solvent ethanol. For use in eq. 9, we note that for the DDM reaction ρ is 0.94 and for acid dissociation ρ is 1.96 where ρ 's are for the benzoic acids in ethanol.² This implies that the electronic demands of the acids in the DDM reaction (degree of bond breaking) are about

one-half of those for simple dissociation. In short, this predicts a common Brønsted $\alpha \approx 0.5$ for eq. 2 for all of the acid families in ethanol.

In drawing lines A, B, and C (Fig. 1 and 2), we gave the points 13 for the 2-methylbenzoic acids no weight so that any nonrandom deviations from the lines due to the proximity effects might be exaggerated. From pK data it is known that as a group the 2-methyl members are generally more acidic in water but slightly less acidic in 50% ethanol than corresponding benzoic acids.^{2,17,30} These pK shifts may be ascribed to steric and solvent factors which include steric effects on conjugation and on solvation of the carboxyl group. In addition, the ρ -data and especially the ρ - ρ plots reveal differentiating rather than constant influences of the o -substituent. For the pK line C, the DDM line B, and the ester hydrolysis line A, the points 13 lie low. In the DDM case this differentiation may be marginal and in fact DDM rate data have been cited as evidence for the "normal" behavior of o -substituted benzoic acids.³¹ Taken together, the data suggest first that the proximity effect of a constant *ortho* group may vary within any family and second that the electronic characteristics of the *ortho* group may effectively enhance or diminish the relay of electronic effects to the reaction site.

If eq. 8 is generally valid, then the preceding discussion suggests a way in which "abnormal" ρ -values may be detected and discussed in the context of the group T or the reaction type. Because of the form of the Hammett equation "exalted" ρ -values are the analogs of exalted σ 's, e.g., $\sigma = 1.27$ for $\sigma = 0.78$ for the p -NO₂ group.² Indeed the low ρ -values for the 2-methylbenzoic system display a "proximity effect" which otherwise might have been missed.

In previous work, ρ -values have sometimes been used to discuss the modes of transmission of electronic effects. For example, inductive, field, and conjugative modes of transmittal of electronic effects have been proposed. Since the ρ - ρ relations test the consistency and validity of the linear free energy relations, they should also provide insights on the relation between structure and ρ . Moreover, it is expected that the abnormal systems may be among the most informative. For this reason, we are examining other families of acids in the DDM reaction 13 to establish the limitations of the ρ - ρ relations.

Experimental

The phenylacetic acids used in this study were purchased or prepared by standard methods. Each acid was decolorized with charcoal if necessary, recrystallized at least twice from water or petroleum ether, and vacuum dried. The presence of traces of mineral acid in the starting material could raise the rate constants; for this reason our acids were recrystallized from neutral solvents. Table IV lists the acids and their properties.

Diphenyldiazomethane was prepared by a standard method and recrystallized repeatedly from methanol at ca. -10° to m.p. 29-30° (lit.^{18c} 29-30°). At $\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{OH}}$ 525 m μ , ϵ_{max} obtained on two separate preparations was 102 ± 1 which differs from the published value of 94 ± 0.5 .^{18c} It is known that DDM decomposes slowly to yield diphenylketazine and tetraphenylethene which do not absorb at 525 m μ .¹⁸ Fortunately, knowledge of ϵ_{max} of DDM was not essential in the rate measurements.

The solvent for the kinetic studies was commercial absolute ethanol.

Pseudo-first-order rate constants for eq. 13 were determined in absolute ethanol by a standard method.^{18,32} The change in optical density of the DDM at 525 m μ , usually ca. 0.8 unit, was followed in a Beckman DK spectrophotometer. The temperature within the reaction cell was held to $\pm 0.1^\circ$. Normally the acid to DDM concentration was greater than 10:1, but in a few runs it was as low as 6:1. The second-order rate constant in-

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TABLE IV
MELTING POINTS AND EQUIVALENTS OF SUBSTITUTED PHENYL-
ACETIC ACIDS

Substituent	Equiv. wt.		M.p., °C.	
	Calcd.	Found	Lit.	Found
H	136.1	135.1	76, 5-77 ^a	77-78
<i>p</i> -I	262.0	259.8	135-136 ^b	139-140
<i>m</i> -I	262.0	256.8	129 ^c	129-130
<i>p</i> -CH ₃ O	166.2	165.6	85-86 ^b	86-87
<i>m</i> -CH ₃ O	166.2	165.1	67 ^d	67-68
<i>p</i> -NO ₂	181.1	180.2	152 ^b	156-157
<i>p</i> -Cl	170.6	167.7	105 ^b	105-106
<i>m</i> -Cl	170.6	169.9	76 ^b	74-75
<i>p</i> -Br	215.1	213.8	114 ^b	113-114
<i>m</i> -Br	215.1	210.8	100 ^e	100-101
<i>p</i> -CH ₃	150.2	147.4	94 ^f	91-92
<i>p</i> -NH ₂	151.2	...	199-200 ^e	200-201
<i>m</i> -NO ₂	181.5	188.6 ^g	120 ^b	117-119

^a A. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 166 (1934).

^b J. F. J. Dippy and F. R. Williams, *ibid.*, 161, 1888 (1934).

^c J. F. J. Dippy, F. R. Williams, and R. H. Lewis, *ibid.*, 644 (1936); 343 (1935). ^d R. Pschorr, *Ann.*, 391, 44 (1912). ^e H. Berger, *J. prakt. Chem.*, 133, 331 (1932). ^f Ref. 22. ^g The quantity available was insufficient for further purification.

creased roughly linearly by ca. 50% in the range 0-1 *M* acid.³³ Therefore the present data are reported for solutions initially ca. 0.0025 *M* in DDM and 0.14 to 0.015 *M* in acid where the deviation from the infinite dilution value was within experimental error. Each acid was usually studied at three different concentrations except as indicated (Table II). The slopes of plots of optical density vs. time gave the pseudo-first-order rate constant which was converted to a second-order constant by division by the initial acid concentration. Additional runs were carried out with comparable phenylacetic acid-DDM concentrations of ca.

(33) R. M. O'Ferrall, unpublished results.

0.015 *M*; the second-order rate constants were calculated directly by another method³³ and agreed with those obtained from the pseudo-first-order runs.

The activation parameters listed in Table II were obtained from the expression³⁴

$$k = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

There is some discrepancy in the reported rate constants for DDM-acid reactions in absolute ethanol. For benzoic acid, the second-order rate constant in 1. mole⁻¹ min.⁻¹ at 30° has been found to be 0.99,³¹ 1.08 (1.04),³⁵ 1.00,³² 1.20²⁸; our interpolated value is 0.99; at 25° the rate constant of Taft and Smith appears to be high at 0.96³⁶; our figure is 0.75 at 26.05°. The Taft and Smith rate constants³⁶ for phenylacetic and phenylpropionic acids are also higher than those found in our laboratory, *i.e.*, 1.47 at 25° vs. 0.81 at 26.05° and 1.01 vs. 0.545 at 25°. It is possible that the total change in optical density in their kinetic runs was too low, *ca.* 0.2 unit or less, and thus susceptible to potential error. Otherwise, our activation parameters indicate that it would require rather improbable errors in the temperature to yield such deviations.

The rate constant for the benzoic acid-DDM reaction increases linearly with the concentration of water (0-8 *M*) added to the ethanol^{18c}; this also appears to hold true for phenylacetic acid.³³ However, the magnitude of this increase is such that the presence of traces of water would not appear to be responsible for these discrepancies in the rate constants. Further, there seems to be no relation between the magnitude of the rate constants and whether the solvent ethanol was redried by the investigators. Until the reasons for these inconsistencies in the DDM-acid reactions are ascertained, some care is needed when the work of different investigators is being compared.

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Structure and Rearrangement of Neutral Phenylketene Dimer¹

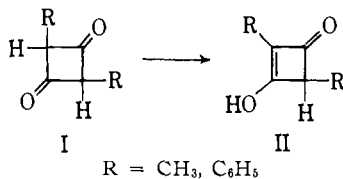
BY JOHN E. BALDWIN² AND JOHN D. ROBERTS

RECEIVED APRIL 2, 1963

Neutral phenylketene dimer has been identified as 3-hydroxy-2,4-diphenyl-3-butenic lactone. It was converted in the presence of base to an acidic isomer, 2,4-diphenylcyclobutenol-3-one.

Introduction

Base-catalyzed rearrangements of neutral phenylketene dimer to an acidic isomer³ and of neutral methylketene dimer to an acidic form⁴ have been reported. These rearrangements were interpreted in terms of conversion of I to II by simple tautomerizations.^{3,4}



Since this early work, investigations of various ketene dimers have led to fairly secure structural assignments for diketene⁵ (IIIa), neutral methylketene and other alkylketene dimers (IIIb),⁶ acidic methyl- and ethylketene dimers (IVb or Vb),⁷ and ketoketene dimers (IVd, IVe).⁸

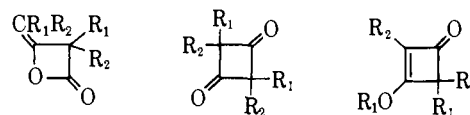
(1) Supported in part by the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1960-1962; Department of Chemistry, University of Illinois, Urbana, Ill.

(3) H. Staudinger, *Ber.*, 44, 533 (1911).

(4) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 42; H. Staudinger, *Ber.*, 63, 1085 (1920).

(5) See V. V. Perekalin and T. A. Sokolva, *Uspekhi Khim.*, 25, 1351 (1956), and R. N. Lacey in "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 240-241, for references to the original structural studies.



IIIa, R₁ = R₂ = H
b, R₁ = H, R₂ = alkyl
c, R₁ = H, R₂ = aryl

IV

Vd, R₁ = R₂ = alkyl
e, R₁ = R₂ = aryl

Two new representatives of this series of compounds have been reported recently: cyclobutane-1,3-dione (which exists as the enol Va)⁹ and 3-hydroxy-2,4-trimethyl-3-pentanoic lactone (IIIId, R = CH₃).¹⁰

From the evidence now available it seems clear that the neutral dimers reported by Staudinger^{3,4} are likely to be lactonic-type dimers and, if so, then the reported

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