

bital theory showed that here the coupling constants could be calculated by considering contributions from magnetic dipolar and electron-orbital terms only.<sup>30</sup> These are likely to be important factors in any analysis of coupling involving only one fluorine also. The apparent dependence of both fluorine-fluorine and pro-

(30) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

ton-fluorine couplings on spatial factors suggests that a mathematical treatment of either phenomenon must also aid our understanding of the other.

**Acknowledgment.**—The author is indebted to Professor M. Karplus, Columbia University, for invaluable correspondence and discussion on sundry theoretical aspects of coupling mechanisms.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILL.]

## The Transmission of Electronic Effects. The $\rho$ - $\rho$ Relation in the Reaction of Phenylpropionic Acids with Diphenyldiazomethane<sup>1</sup>

BY RORY A. MORE O'FERRALL AND SIDNEY I. MILLER

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Rate data for the reactions of ten phenylpropionic acids (*p*-(CH<sub>3</sub>)<sub>2</sub>CH, *p*-CH<sub>3</sub>, *p*-CH<sub>3</sub>O, 3,4-(CH<sub>3</sub>O)<sub>2</sub>, H, *p*-F, *m*-HO, *p*-Br, *m*-Cl, *p*-NO<sub>2</sub>) with diphenyldiazomethane (DDM) in ethanol have been obtained. The entropies of activation ( $-\Delta S^*$  = 6–15 e.u.) are proportional to the enthalpies of activation ( $\Delta H^*$  = 12.7–15.4 kcal. mole<sup>-1</sup>) in this series with a slope of *ca.* 260°. Acceptable Hammett lines have been obtained for *k* in l. mole<sup>-1</sup> min.<sup>-1</sup> at 26.05°,  $\log k = 0.18\sigma - 0.226$  and at 35.35°,  $\log k = 0.17\sigma + 0.1105$ . Taking  $\rho$  from the dissociation of the acids RCOOH and  $\rho'$  from the rate constants of these acids with DDM, one obtains satisfactory test comparisons in the form  $\rho/\rho' = \text{constant}$ . Alternatively, the attenuation factor for phenylpropionic acids or esters relative to corresponding benzoic derivatives is  $\epsilon = 0.22$  for four different reactions. Despite their utility, it does not yet seem possible to provide a rigorous theoretical basis for these  $\rho$ - $\rho$  relations.

In this paper we continue our inquiry into the factors which affect the relay of electronic influences from a substituent R to a reaction site S in a species R-G<sub>i</sub>-COS. Previously, it was shown that two substantially equivalent  $\rho$ - $\rho$  relations

$$\rho_{R-G-COOH}/\rho_{R-G-COS} = \pi \quad (1)$$

$$\rho_{R-G-COS}/\rho_{RC_6H_4COS} = \epsilon \quad (2)$$

were useful in examining the alterations in the Hammett  $\rho$  as the reaction type changed but the interposed group G remained the same (eq. 1), or as the reaction type remained unchanged but the interposed group G varied (eq. 2).<sup>2-5</sup>  $\pi$  is a measure of the ability of a substituent to communicate electronic effects to a given site for a given reaction (*e.g.*, ester hydrolysis compared to a standard reaction, *i.e.*, acid dissociations in water at 25°) and  $\epsilon$  is a measure of the attenuation of an electronic effect through G as compared with the group -C<sub>6</sub>H<sub>4</sub>.<sup>4-6</sup>

Together with acid dissociation of acids RCOOH or the basic hydrolysis of their esters, the reactions of the acids with diphenyldiazomethane (DDM) have attained the status of a standard or probe process in structure reactivity studies.<sup>3-5,7</sup> To test eq. 1 and 2 we have accumulated rate data on several acid families

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

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

(3) R. A. M. O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963).

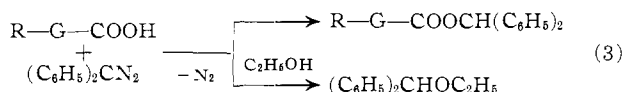
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(5) W. K. Kwok, R. A. More O'Ferrall, and S. I. Miller, *Tetrahedron*, **20**, 1913 (1964).

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in this reaction



Here rate data are reported for several phenylpropionic acids in process 3 and the problem of attenuation of the substituent effect by G is considered. Because its reaction site is "insulated" from the substituent, the phenylpropionic system is of particular interest in theories of the influence of structure on reactivity.

### Results and Discussion

Rate data for the reactions of the phenylpropionic acids with DDM are given in Table I. For a wide range

TABLE I  
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION:

R	$-k$ , l. mole <sup>-1</sup> min. <sup>-1</sup> <sup>a,b</sup>		$\Delta H^* \pm 1.0$ , cal. deg. <sup>-1</sup> $-\Delta S^* \pm 3.0$ , cal. deg. <sup>-1</sup> <sup>c</sup>	
	26.05 ± 0.1°	35.35 ± 0.1°	kcal. mole <sup>-1</sup>	mole <sup>-1</sup>
<i>p</i> -i-C <sub>3</sub> H <sub>7</sub>	0.52			
<i>p</i> -CH <sub>3</sub>	.54	1.18	14.4	9.3
<i>p</i> -CH <sub>3</sub> O	.56	1.11	12.7	14.9
3,4-(CH <sub>3</sub> O) <sub>2</sub>	.55	1.22	15.0	7.3
H	.58 <sup>c</sup>	1.21	13.7	11.5
<i>p</i> -F	.63			
<i>m</i> -HO	.54	1.22	15.4	5.7
<i>p</i> -Br	.64	1.44	15.3	6.4
<i>m</i> -Cl	.68	1.50	15.0	7.7
<i>p</i> -NO <sub>2</sub>	.85	1.77	13.6	12.7

<sup>a</sup> Average deviation less than 2%. <sup>b</sup> Average of three runs except as indicated. <sup>c</sup> Average of four runs.

of substituents the total variation in the rates is small at 1.6. As in the DDM reactions with the phenylacetic<sup>3</sup> and *trans*-cinnamic<sup>4</sup> acids the activation entropies and enthalpies are proportional; here the slope

is *ca.* 260°. Our determination of the activation parameters, which were not of primary interest, derives from two temperatures, so the entropy-enthalpy relation can only be tentative.

The results of correlating  $\log k$  with  $\sigma$ -values based on the dissociation of the benzoic acids<sup>8a</sup> or with "resonance-free"  $\sigma^n$  values<sup>8b</sup> are given in Table II.

TABLE II  
LINEAR CORRELATIONS FOR THE REACTIONS OF  
PHENYLPROPIONIC ACIDS WITH DIPHENYLDIAZOMETHANE

Temp., °C.	$\sigma^{18}$	$\rho$	$\log k,^a$	$s^b$	$r^c$	$n^d$
26.05	$\sigma$	0.18	-0.226	0.0030	0.96	10
	$\sigma^n$	.21	-.243	.0034	.95	8
35.35	$\sigma$	.17	.1105	.0029	.96	8
	$\sigma^n$	.22	.859	.0013	.98	8

<sup>a</sup> Intercept of Hammett equation. <sup>b</sup> Standard deviation. <sup>c</sup> Correlation coefficient. <sup>d</sup> Number of compounds used in correlation.

Both correlations are adequate although a Hammett plot, not shown, reveals typical scatter. The  $\rho$  based on the present DDM data holds up well when tested in eq. 1; figures showing the development of this  $\rho$ - $\rho$  relation are given elsewhere.<sup>3-5</sup> Relative to the standard  $\rho$ -values for dissociation of the acids *in water* at 25°, the efficiency of transmission of electronic effects to the site of the DDM reaction *in ethanol* at 30° is *ca.* 90%, or  $\rho_{\text{RGCOS}}/\rho_{\text{RGCOS}} \approx 0.9$ .

Otherwise, eq. 2 can be used. Making the comparison between the phenylpropionic and the benzoic systems in the four reactions—acid dissociation in water, acid dissociation in 50% ethanol, basic hydrolysis of the ethyl esters in 88% ethanol at 30°, and acid and DDM in ethanol at 30°<sup>2,3,9</sup>—one obtains  $\rho_{\text{ArCH}_2\text{CH}_2\text{COS}}/\rho_{\text{ArCOS}} = 0.212, 0.23, 0.20, \text{ and } 0.22$ , respectively. That is, in any reaction, the two methylene groups of the phenylpropionic system have cut the transmission to 22% of that in the benzoic acids, or  $\epsilon = 0.22$ . Either viewpoint of eq. 1 or 2 means of course that G is damping out the relay of electronic effects in a completely predictable manner. Clearly, the phenylpropionic system is now close to the lower limit of transmission efficiency among available families<sup>2,3</sup>; by contrast, the high end of the  $\rho$ -scale is found in the furoic acid series.<sup>5</sup>

Apart from the experimental approach of eq. 1 and 2, it would be desirable to estimate attenuation factors ( $\epsilon$ ) independently. If field-effect theory is to be applicable at all, it should apply to series in which conjugation between the substituent and the reaction site is precluded. The relation between attenuation and the Kirkwood-Westheimer (K.W.) theory<sup>10</sup> takes the form<sup>4</sup>

$$\epsilon = \rho/\rho' = \left( \frac{\cos \theta}{r^2 D_E} \right) / \left( \frac{\cos \theta'}{r'^2 D_{E'}} \right) \quad (4)$$

A comparison of  $\rho$ -values for the phenylacetic and phenylpropionic families in three reaction types—acid dissociation in water, basic hydrolysis of ethyl esters in

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(10) (a) J. G. Kirkwood and F. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938); (b) F. Westheimer, *J. Am. Chem. Soc.*, **61**, 1977 (1939); **62**, 1892 (1940); (c) C. Tanford, *ibid.*, **79**, 5348 (1957); (d) C. D. Ritchie and E. S. Lewis, *ibid.*, **84**, 591 (1962).

88% ethanol, and reaction of DDM with the acids in ethanol—leads to  $\epsilon$ -values of 0.41, 0.61, and 0.49, respectively<sup>3</sup>; K.W. theory leads to  $\epsilon$ -values of 0.52, 0.77, and 0.77, respectively.<sup>4,10b,11</sup>

The discrepancies between the experimental fall-off factor contained in the  $\rho$ - $\rho$  relation and those produced by theory are not trivial but certainly no larger than what one has learned to expect from K.W. theory.<sup>10</sup> When a resonance interaction between the substituent and the reaction site is possible, *e.g.*, in the cinnamic acids, the discrepancy is somewhat larger.<sup>4</sup> Even when the theory was modified to correct for systems with conjugation,<sup>13</sup> the results were not wholly satisfactory.<sup>4</sup>

Both K.W. theory and the Dewar-Grisdale elaboration of it give approximate estimates of the transmission of electronic effects in chemical systems. In taking into account detailed changes in molecular geometry ( $r, \theta$ ) and medium ( $D_E$ ), K.W. theory predicts that for any given G in RGCOS the attenuation factor ( $\epsilon$ ) should vary with the medium.<sup>10</sup> On the other hand, the  $\rho$ - $\rho$  relations, eq. 1 and 2, were derived on the basis that  $\epsilon$  does not vary with the reaction or the medium.<sup>3,4</sup> Although these two approaches are clearly inconsistent, it does not seem possible to estimate how important the difference may be in any given case. The available experimental data indicate that the families RGCOS, with few exceptions, fit the  $\rho$ - $\rho$  relations.<sup>14</sup> This of course justifies the judicious application of  $\rho$ - $\rho$  relations until such time as they have outlived their usefulness.

## Experimental

The procedure used in studying the reaction of DDM with the phenylpropionic acids and the treatment of the kinetic data have been described.<sup>3,4</sup> The properties of the acids are given in Table

TABLE III  
THE PHENYLPROPIONIC ACIDS

Substituent	—Equiv. wt.—		—M.p., °C.—	
	Calcd.	Found	Lit.	Found
<i>p</i> -Br	229.1	232.1	136 <sup>b</sup>	137-138
3,4-(CH <sub>3</sub> O) <sub>2</sub>	210.2	213.7	98 <sup>b</sup>	97-98
<i>m</i> -HO	166.2	163.7	111 <sup>c</sup>	113-114
H	150.2	150.8	48.5-49.5 <sup>a</sup>	48.5-49.5
<i>p</i> -CH <sub>3</sub>	164.2	165.3	116.5-117 <sup>a</sup>	115.5-116.5
<i>p</i> -i-C <sub>3</sub> H <sub>7</sub>	192.2	192.6	73 <sup>d</sup>	74-75
<i>p</i> -F	168.2	169.1	91 <sup>b</sup>	85.5-87
<i>m</i> -Cl	184.6	185.7	73-74 <sup>e</sup>	71.5-72.5
<i>p</i> -NO <sub>2</sub>	195.2	199.6	166-167 <sup>a</sup>	168.5-170
<i>p</i> -CH <sub>3</sub> O	180.2	180.1	107-108 <sup>a</sup>	100.5-102

<sup>a</sup> E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 401 (1958). <sup>b</sup> K. Kindler and T. Li, *Ber.*, **74**, 321 (1941). <sup>c</sup> F. Tiemann and R. Ludwig, *ibid.*, **15**, 2043 (1882). <sup>d</sup> G. H. Slotka and H. Heller, *ibid.*, **63**, 3029 (1930). <sup>e</sup> J. Kenner and E. Witham, *J. Chem. Soc.*, 119, 1452 (1921).

(11) For a critical appraisal of K.W. theory see ref. 10c; for the problem of solvation of substituents and K.W. theory see ref. 10d. The problem of uncertain geometry in the phenylpropionic acid side chain is no longer a matter of concern. The acidities of  $\beta$ -substituted propionic acids were recently compared with those of a bicyclic system, 3-*endo*- or 3-*exo*-R-bicyclo-[2.2.1]hept-5-ene-2-*endo*-carboxylic acid, in which the substituent (R) and the carboxyl group were fixed either in a *cis* or *trans* structure.<sup>12</sup> Plots of the  $pK$  values of the propionic acids were linearly related to corresponding acids in the *trans* series with a slope =  $0.90 \pm 0.1$  but did not correlate with those of the *cis* series.<sup>12</sup> This strongly suggests that the *trans* conformation is favored by the phenylpropionic acids.

(12) H. Hogeveen and F. Montanari, *J. Chem. Soc.*, 4864 (1963).

(13) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

(14) This statement applies to families covered by the Hammett equation. Unpublished work shows that attenuation factors obtained for families covered by the Taft equation are much more variable.

III. A Beckman DK spectrophotometer was used in this work. Kinetic data were taken at  $35.35 \pm 0.1^\circ$  and at different temperatures held to  $\pm 0.1^\circ$  in the range  $25.5$ – $26.2^\circ$ . Activation energy plots permitted the adjustment of the rate constants to a common temperature  $26.05 \pm 0.1^\circ$  given in Table I; in no case was the correction greater than 4%. The DDM concentration at *ca.*  $0.0022 M$  was normally in the range  $1/10$  to  $1/80$  of the

acid so that pseudo-first-order kinetics applied; two runs at a ratio of  $1/6$  are still acceptable for the pseudo-first-order treatment since only *ca.* 60% of the DDM reacts to give the ester (see eq. 3). All of the kinetic data are given in Table I.

**Acknowledgment.**—We wish to thank J. Belluzzi for preparing several of the acids.

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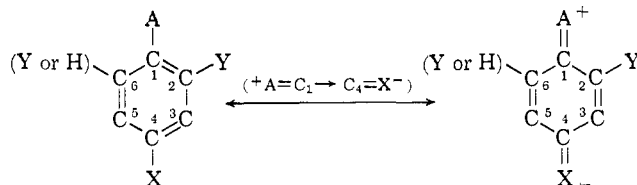
## Steric Enhancement of Resonance. II. Absorption Spectra of N-Alkyl- and N,N-Dialkyl-2,4-dinitroanilines<sup>1,2</sup>

BY MORTIMER J. KAMLET, HORST G. ADOLPH, AND JOHN C. HOFFSOMMER

RECEIVED APRIL 27, 1964

Close comparison of the ultraviolet spectra of 2,4-dinitroaniline (I) and its N-alkyl and N,N-dialkyl derivatives allows one to discern the spectral effects of *steric enhancement of* ( $+R_2N=C_1 \rightarrow C_4=NO_2^-$ ) resonance as well as steric inhibition of ( $+R_2N=C_1 \rightarrow C_2=NO_2^-$ ) resonance. The existence of another hitherto undescribed phenomenon, *the electronic buttressing effect*, is suggested to explain some of the spectral variations.

*Steric diminution of electronic suppression of resonance interaction* or, more succinctly, *steric enhancement of resonance* may occur in a system such as the following where, in Ingold's notation,<sup>3</sup> A is a +M or +I substituent and X and Y are -M substituents. A measure



of resonance interaction between A and X (or between C<sub>1</sub> and X where A is a +I substituent) is the electronic transition energy of the ( $+A=C_1 \rightarrow C_4=X^-$ ) band in the ultraviolet. This transition energy depends strongly on the ground-state electron density at A,  $\lambda_{\max}$  shifting to the red with increasing electron density at A, to the blue with decreasing electron density.

The ground-state electron density at A is, in turn, a strong function of the nature of Y and its degree of coplanarity with the ring. Coplanar Y effects both mesomeric and inductive electron withdrawal from A, thereby suppressing resonance interaction between A and X; noncoplanar Y exerts only its inductive effect,<sup>4</sup> also suppressing A→X resonance interaction, but to a lesser extent.

It follows that as progressively increasing steric requirements of A force Y from coplanarity, ground-state electron withdrawal from A by Y will decrease and resonance interaction between A and X will increase. As concerns A→Y resonance interaction, this is the classical situation of steric inhibition of resonance. In the case of A→X resonance interaction, however, the newly reported phenomenon,<sup>1</sup> *steric*

*enhancement of resonance*, is being brought into play. It is an important corollary of the above that *steric enhancement of resonance in one molecular axis is always accompanied by steric inhibition of resonance in another molecular axis*.

We have reported that steric enhancement of resonance is evidenced by progressive bathochromic spectral displacements in the series [2,4,6-trinitrotoluene, 1-ethyl-2,4,6-trinitrobenzene, 1-isopropyl-2,4,6-trinitrobenzene, 1-*t*-butyl-2,4,6-trinitrobenzene]<sup>1</sup> and [2,4-dinitrotoluene, 1-ethyl-2,4-dinitrobenzene, 1-isopropyl-2,4-dinitrobenzene, 1-*t*-butyl-2,4-dinitrobenzene].<sup>5</sup> We wish now to demonstrate that this phenomenon also obtains with the N,N-dialkyl-2,4-dinitroanilines and may be discerned on detailed examination of the ultraviolet spectra of these and related compounds.

**Band Assignments.**—The spectrum of 2,4-dinitroaniline (I) above 280  $m\mu$  comprises a high intensity N → V band,  $\lambda_{\max}$  336  $m\mu$ , upon whose longer wave length edge is superimposed a pronounced shoulder,  $\lambda \sim 390 m\mu$  (Table I, Fig. 1). The spectral envelope appears to result from the fusion of two bands: (1)  $\lambda_{\max}$  333–336  $m\mu$  ( $\epsilon$  13,500–14,000); (2)  $\lambda_{\max}$  380–390  $m\mu$  ( $\epsilon$  4000–5000). Since higher absorption intensities are generally associated with longer transition moments, it is reasonable to couple band 1 with the ( $+H_2N=C_1 \rightarrow C_4=NO_2^-$ ) electronic transition, band 2 with the ( $+H_2N=C_1 \rightarrow C_2=NO_2^-$ ) transition.

Comparison of the spectrum of I with those of other mono- and polynitroanilines lends strength to these band assignments. An ( $+H_2N=C_1 \rightarrow C_2=NO_2^-$ ) electronic transition in 2-nitroaniline leads to  $\lambda_{\max}$  404  $m\mu$  ( $\epsilon$  5200); 2,6-dinitroaniline, with electronic transitions of this type in two mutually equivalent molecular axes, shows  $\lambda_{\max}$  412  $m\mu$  ( $\epsilon$  9200). 4-Nitroaniline, on the other hand, shows higher intensity absorption characteristic of an ( $+H_2N=C_1 \rightarrow C_4=NO_2^-$ ) electronic transition,  $\lambda_{\max}$  371  $m\mu$  ( $\epsilon$  15,900). 2,4,6-Trinitroaniline, with one *para* electronic transition and two mutually equivalent *ortho* transitions, shows two distinct bands,  $\lambda_{\max}$  318  $m\mu$  ( $\epsilon$  12,000), and  $\lambda_{\max}$  408  $m\mu$  ( $\epsilon$  7800).

(5) Part III: M. J. Kamlet, H. G. Adolph, and B. Johnson, manuscript in preparation.

(1) Part I: M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, *J. Am. Chem. Soc.*, **84**, 3925 (1962).

(2) V. Baliah and M. Uma [*Tetrahedron Letters*, No. 25, 21 (1960)] had used the term, *steric enhancement of resonance*, to describe the effect of a 2-alkyl group in increasing the probability of alkoxy or alkylthio groups approaching coplanarity in such compounds as 2-methyl-4-nitroanisole or methyl 2-methyl-4-nitrophenyl sulfide. Although the same term adequately describes both sets of phenomena, the phenomena themselves are somewhat different. We regret that Baliah and Uma's paper had not come to our attention prior to the publication of Part I.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Section 7.

(4) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958)