

## Kinetics of the Reactions of Biphenyl-4-carboxylic Acids and 1-Naphthoic Acids with Diazodiphenylmethane in Various Alcohols

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Rate constants have been determined for the reactions at 30, 35, and 40 °C of diazodiphenylmethane with 4'-substituted biphenyl-4-carboxylic acids and 4-substituted 1-naphthoic acids in 14 alcohols. Hammett  $\rho$  values have been evaluated for the reactions in 11 of the alcohols. The log  $k$  values for reactions of biphenyl-4-carboxylic acid and 1-naphthoic acid in the 14 alcohols are linearly related to the corresponding values for benzoic acid. Multiple correlations of log  $k$  with groups of suitable solvent parameters are very successful. The dielectric effect has a negative influence on  $\rho$  values which decrease with temperature. The transmission of electronic effects through the biphenyl ring system is compared with that in benzene.

THE esterification of carboxylic acids with diazodiphenylmethane has been extensively studied spectrophotometrically by Chapman *et al.*<sup>1-12</sup> Although the influence of solvents on this reaction involving benzoic acids,<sup>6</sup> phenylacetic acids,<sup>8</sup> and *trans*-cinnamic acids<sup>11</sup> has been thoroughly investigated, no such similar study has so far been exclusively devoted to biphenylcarboxylic and naphthoic acids. Hence we have studied the kinetics of the reactions of 4'-substituted biphenyl-4-carboxylic acids and 4-substituted 1-naphthoic acids in several alcohols to elucidate the influence of solvents on rate and also on the Hammett  $\rho$  constant.

### EXPERIMENTAL

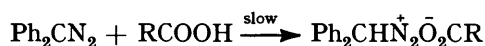
**Materials.**—The acids were prepared by the hypochlorite oxidation of the corresponding methyl ketones.<sup>13-15</sup> Diazodiphenylmethane was prepared by the method of Schroeder and Katz<sup>16</sup> and stored in a refrigerator. The solvents were purified by standard methods<sup>17-20</sup> and their purity was tested by g.l.c.

**Rate Measurements.**—In the presence of an excess of acid, the reaction is of the first order. Pseudo-first-order rate constants were determined spectrophotometrically by Smith and Hunt's method.<sup>21</sup> Optical density measurements were taken at 525 nm with 10 mm cells in a Perkin-Elmer-Hitachi 200 u.v.-visible spectrophotometer. The apparent second-order rate constants were calculated by dividing the pseudo-first-order rate constants by the acid concentration.

**Correlations.**—Multiple correlations with several solvent parameters were carried out at the University of Tennessee, Knoxville, U.S.A., with an IBM 370/3031 computer using the SAS 79 program GLM.

### RESULTS AND DISCUSSION

The mechanism of reaction between a carboxylic acid and diazodiphenylmethane involves rate-determining proton transfer from the acid to diazodiphenylmethane to form a diphenylmethanediazonium carboxylate ion-pair.<sup>10, 22, 23</sup> The kinetic results obtained in the



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present study are given in Tables 1–3. The log  $k$  values ( $k$  is the rate constant for the parent acid at 30 °C) in all the alcohol solvents show a linear correlation with the corresponding values, taken from the literature,<sup>6</sup> for the reactions of benzoic acid with diazodiphenylmethane at 30 °C with correlation coefficient  $r$  of 0.993 and standard deviation  $s$  of 0.044 for biphenyl-4-carboxylic acid and with  $r$  0.994 and  $s$  0.034 for 1-naphthoic acid. Such linear free-energy correlations indicate that the same solvent properties act on the reactions of the acids correlated and that the influence of a given solvent property on one reaction is proportional to its influence on the other.

**Dependence of the Rate Constants on the Properties of Alcohols used as Solvent at 30 °C.**—Since the mechanism of the reaction involves the formation of an ion-pair intermediate, one may expect the rate to increase with increase in polarity of the solvent.<sup>24</sup> Hence we desired to see if any correlation existed between the rate and the dielectric constant,  $\epsilon$ , or  $1/\epsilon$ , or the Kirkwood function<sup>25</sup> of the dielectric constant,  $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$ . In all these cases the correlations were extremely poor. The correlation of log  $k$  with  $\sigma^*$ , the polar substituent constant of the alkyl group<sup>26</sup> of the alcohol, was only satisfactory with  $r$  0.954 and 0.955 for biphenyl-4-carboxylic acid and 1-naphthoic acid, respectively. This made us seek multiple correlations of log  $k$  with several solvent parameters. In the work of Chapman *et al.*<sup>8</sup> with ten alcohols, a multiple linear correlation of log  $k$  with  $f(\epsilon)$  and  $\sigma^*$  achieved considerable success, and hence we decided that an analogous correlation would be an appropriate starting point for the alcohols in the present study.

Expression (1) was obtained for biphenyl-4-carboxylic acid with  $R$  0.969 and  $s$  0.120,  $R$  being the multiple correlation coefficient and  $s$  the standard deviation.

$$\log k = -1.584 + 4.345 f(\epsilon) + 2.657 \sigma^* \quad (1)$$

$$(\pm 1.416) \quad (\pm 0.224)$$

The corresponding expression for 1-naphthoic acid is (2) with  $R$  0.981 and  $s$  0.060. Although statistical analysis reveals that equations (1) and (2) are much

$$\log k = -1.380 + 4.148 f(\epsilon) + 2.789 \sigma^* \quad (2)$$

$$(\pm 1.156) \quad (\pm 0.183)$$

TABLE 1

Rate constants ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ ) for the reactions of 4'-substituted biphenyl-4-carboxylic and 4-substituted 1-naphthoic acids with diazodiphenylmethane in alcohols at 30 °C

Solvent	Biphenyl-4-carboxylic acid				1-Naphthoic acid			
	4'-CH <sub>3</sub>	4'-H	4'-Br	4'-NO <sub>2</sub>	4-CH <sub>3</sub>	4-H	4-Br	4-HO <sub>2</sub>
1 Methanol	2.30	2.50	2.83	3.76	3.01	3.83	6.26	14.09
2 Ethanol	0.93	1.02	1.16	1.57	1.18	1.54	2.58	6.44
3 Propan-1-ol	1.22	1.32	1.53	2.10	1.29	1.71	3.00	7.61
4 Propan-2-ol	0.64	0.71	0.83	1.17	0.77	1.06	2.01	5.71
5 Butan-1-ol	1.12	1.23	1.41	1.92	0.98	1.31	2.34	6.09
6 2-Methylpropan-1-ol	1.96	2.15	2.46	3.40	1.76	2.30	3.95	9.67
7 Butan-2-ol	0.86	0.95	1.08	1.49	0.72	0.96	1.72	4.48
8 2-Methylpropan-2-ol	0.28	0.32	0.38	0.59	0.33	0.47	0.94	2.92
9 Pentan-1-ol	1.09	1.20	1.37	1.88	0.83	1.11	2.00	5.27
10 Benzyl alcohol	8.41	9.10	10.11	12.99	10.31	12.91	20.20	(15.61) *
11 2-Methylbutan-2-ol	0.13	0.15	0.18	0.29	0.13	0.19	0.44	1.73
12 Cyclopentanol		0.88				0.98		
13 1-Phenylethanol		3.70				5.05		
14 2-Phenylethanol		2.95				4.15		

\* Value with 4-fluoro-1-naphthoic acid.

TABLE 2

Rate constants ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ ) for the reactions of 4'-substituted biphenyl-4-carboxylic and 4-substituted 1-naphthoic acids with diazodiphenylmethane in alcohols at 35 °C

Solvent	Biphenyl-4-carboxylic acid				1-Naphthoic acid			
	4'-CH <sub>3</sub>	4'-H	4'-Br	4'-NO <sub>2</sub>	4-CH <sub>3</sub>	4-H	4-Br	4-NO <sub>2</sub>
1 Methanol	3.11	3.36	3.74	4.81	4.42	5.56	8.82	18.88
2 Ethanol	1.30	1.42	1.60	2.11	1.83	2.29	3.59	7.53
3 Propan-1-ol	1.76	2.04	2.31	3.11	2.02	2.56	4.11	9.01
4 Propan-2-ol	0.91	1.01	1.16	1.61	1.19	1.60	2.92	7.85
5 Butan-1-ol	1.73	1.85	2.09	2.79	1.62	2.06	3.37	7.58
6 2-Methylpropan-1-ol	2.74	3.01	3.40	4.55	3.09	3.87	6.07	12.77
7 Butan-2-ol	1.18	1.29	1.46	1.95	1.23	1.57	2.57	5.78
8 2-Methylpropan-2-ol	0.41	0.46	0.55	0.82	0.51	0.69	1.30	3.38
9 Pentan-1-ol	1.54	1.68	1.90	2.54	1.30	1.67	2.75	6.24
10 Benzyl alcohol	11.60	12.45	13.70	17.26		16.75		
11 2-Methylbutan-2-ol	0.19	0.22	0.27	0.41	0.22	0.32	0.65	2.12
12 Cyclopentanol		1.35				1.58		
13 1-Phenylethanol		5.58				7.27		
14 2-Phenylethanol		4.52				6.11		

TABLE 3

Rate constants ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ ) for the reactions of 4'-substituted biphenyl-4-carboxylic and 4-substituted 1-naphthoic acids with diazodiphenylmethane in alcohols at 40 °C

Solvent	Biphenyl-4-carboxylic acid				1-Naphthoic acid			
	4'-CH <sub>3</sub>	4'-H	4'-Br	4'-NO <sub>2</sub>	4-CH <sub>3</sub>	4-H	4-Br	4-NO <sub>2</sub>
1 Methanol	4.91	5.27	5.80	7.28	6.83	8.22	11.90	22.03
2 Ethanol	2.02	2.18	2.43	3.12	2.69	3.22	4.61	8.36
3 Propan-1-ol	2.96	3.21	3.60	4.70	3.09	3.74	5.48	10.32
4 Propan-2-ol	1.28	1.41	1.60	2.17	1.63	2.18	3.92	10.30
5 Butan-1-ol	2.64	2.86	3.20	4.17	2.53	3.09	4.61	8.95
6 2-Methylpropan-1-ol	3.93	4.27	4.78	6.26	4.31	5.16	7.41	13.47
7 Butan-2-ol	1.66	1.80	2.01	2.62	1.72	2.10	3.14	6.09
8 2-Methylpropan-2-ol	0.58	0.65	0.76	1.11	0.79	1.02	1.70	3.94
9 Pentan-1-ol	2.25	2.44	2.73	3.56	1.85	2.26	3.40	6.67
10 Benzyl alcohol	16.56	17.63	19.25	23.44		22.80		
11 2-Methylbutan-2-ol	0.28	0.32	0.37	0.57	0.34	0.45	0.81	2.47
12 Cyclopentanol		1.80				2.16		
13 1-Phenylethanol		7.50				9.71		
14 2-Phenylethanol		6.05				8.30		

better, they do not predict the correct order of reactivity (Table 4). In our attempt to improve the situation we introduced the parameter  $L$ , the solubility of hydrogen chloride in the alcohol,<sup>27</sup> as an alternative to  $\sigma^*$  but

could not use it due to non-availability of  $L$  for all the alcohols.

The parameter  $\sigma^*$  shows only a low degree of collinearity with  $E_s$ , the Taft steric constant ( $r \text{ ca. } 0.37$ ) and

hence we feel that a possible contribution from  $E_s$  is worth analysing. Equation (3) is found with  $R$  0.979 and  $s$  0.102 for biphenyl-4-carboxylic acid and equation

$$\log k = -3.983 + 9.379 f(\epsilon) + 3.043 \sigma^* - 0.255E_s \quad (3)$$

$(\pm 2.543) \quad (\pm 0.257) \quad (\pm 0.114)$

(4) with  $R$  0.990 and  $s$  0.05 for 1-naphthoic acid. While (3) and (4) are statistically superior to (1) and (2) they do

$$\log k = -2.094 + 5.746 f(\epsilon) + 3.502 \sigma^* - 0.160E_s \quad (4)$$

$(\pm 1.065) \quad (\pm 0.285) \quad (\pm 0.059)$

not predict the exact order of reactivity. Notably they fail to account for the higher rate constants (Table 4) in 2-methylpropan-1-ol. A similar situation was encountered by Chapman *et al.*<sup>8</sup> for benzoic acid and they suggested that the behaviour may be connected with branching at the  $\beta$ -carbon atom and they successfully dealt with the anomalous effect of this branching in terms of a third parameter,  $n \gamma$ -H, the number of  $\gamma$ -hydrogen atoms.<sup>9</sup> Following their approach, when  $n \gamma$ -H is introduced in place of  $E_s$ , the correlation yielded equation (5) with  $R$  0.988 and  $s$  0.079 for biphenyl-4-

$$\log k = -1.690 + 4.481 f(\epsilon) + 2.876 \sigma^* + 0.0492 n \gamma\text{-H} \quad (5)$$

$(\pm 0.986) \quad (\pm 0.159) \quad (\pm 0.0126)$

carboxylic acid and the corresponding expression (6) for 1-naphthoic acid with  $R$  0.994 and  $s$  0.034. Indeed

$$\log k = -1.799 + 4.645 f(\epsilon) + 2.967 \sigma^* + 0.0301 n \gamma\text{-H} \quad (6)$$

$(\pm 0.954) \quad (\pm 0.161) \quad (\pm 0.0128)$

$\sigma^*$  is not collinear with  $n \gamma$ -H ( $r$  ca. 0.15). Thus, the  $n \gamma$ -H parameter appears, from the statistical success, to be much better than  $E_s$  as a measure of steric influence on the solvent effect. The remarkable success of (5) lies not only in its ability to predict a nearly correct value for 2-methylpropan-1-ol but also the order of reactivity. In the case of 1-naphthoic acid equation (6) does not

have a much better claim than equation (4) when 2-methylpropan-1-ol is concerned.

Our results produce equations (7) and (8) at 35 and 40 °C respectively for biphenyl-4-carboxylic acid. The

$$\log k = -1.659 + 4.810 f(\epsilon) + 2.826 \sigma^* + 0.0415 n \gamma\text{-H} \quad (7)$$

$(\pm 0.762) \quad (\pm 0.129) \quad (\pm 0.0103)$   
 $(R 0.992, \quad s 0.064)$

$$\log k = -1.453 + 4.650 f(\epsilon) + 2.851 \sigma^* + 0.0506 n \gamma\text{-H} \quad (8)$$

$(\pm 0.759) \quad (\pm 0.129) \quad (\pm 0.0102)$   
 $(R 0.992, \quad s 0.064)$

analogous equations for 1-naphthoic acid are (9) and (10).

$$\log k = -1.309 + 4.292 f(\epsilon) + 2.8080 \sigma^* + 0.0342 n \gamma\text{-H} \quad (9)$$

$(\pm 0.859) \quad (\pm 0.145) \quad (\pm 0.016)$   
 $(R 0.990, \quad s 0.050)$

$$\log k = -1.254 + 4.489 f(\epsilon) + 2.755 \sigma^* + 0.0313 n \gamma\text{-H} \quad (10)$$

$(\pm 0.835) \quad (\pm 0.141) \quad (\pm 0.0112)$   
 $(R 0.987, \quad s 0.060)$

#### Variation of the Hammett $\rho$ Constant with Solvent.—

The Hammett  $\rho$  values for the reactions of 4-substituted-1-naphthoic acids are given in Table 5. In benzyl alcohol, 4-nitro-1-naphthoic acid underwent a very fast reaction and in this solvent 4-fluoro-1-naphthoic acid was used instead of 4-nitro-1-naphthoic acid for evaluating  $\rho$ . The  $\rho$  values of the reactions of 4-substituted-1-naphthoic acids are linearly related to the corresponding  $\rho$  values of the reactions of *meta*-substituted benzoic acids<sup>6,9</sup> in eight of the alcohols with  $r$  0.996 and  $s$  0.034. A similar correlation exists for 4'-substituted biphenyl-4-carboxylic acids with  $r$  0.995 and  $s$  0.036. These correlations show that the factors which govern the  $\rho$  values in these three systems are closely related. The  $\rho$  values are found to decrease with temperature as expected.

It was considered of interest to examine how solvent

TABLE 4  
Multiple correlation with various solvent parameters of  $\log k$  at 30 °C

Solvent	Biphenyl-4-carboxylic acid $\log k$				1-Naphthoic acid $\log k$			
	Obs.	Calc. (1)	Calc. (3)	Calc. (5)	Obs.	Calc. (2)	Calc. (4)	Calc. (6)
1 Methanol	0.398	0.490	0.495	0.449	0.583	0.600	0.649	0.518
2 Ethanol	0.009	0.192	0.137	0.128	0.188	0.290	0.267	0.187
3 Propan-1-ol	0.121	0.125	0.107	0.204	0.233	0.222	0.225	0.103
4 Propan-2-ol	-0.149	-0.090	-0.126	-0.175	0.025	0.001	-0.041	-0.126
5 Butan-1-ol	0.090	0.058	0.011	0.084	0.117	0.155	0.141	0.100
6 2-Methylpropan-1-ol	0.332	0.007	0.177	0.302	0.362	0.175	0.253	0.242
7 Butan-2-ol	-0.022	-0.169	-0.076	-0.112	-0.018	-0.089	-0.049	-0.130
8 2-Methylpropan-2-ol	-0.495	-0.465	-0.367	-0.577	-0.328	-0.388	-0.365	-0.541
9 Pentan-1-ol	0.079	0.017	-0.076	0.042	0.045	0.115	0.088	0.056
10 Benzyl alcohol	0.959	0.920	0.929	0.922	1.111	1.065	1.276	1.116
11 2-Methylbutan-2-ol	-0.824	-0.495	-0.711	-0.727	-0.721	-0.665	-0.644	-0.759
12 Cyclopentanol	-0.056	-0.008	-0.047	-0.085	-0.009	-0.087	0.074	-0.033
13 1-Phenylethanol	0.568	0.521	0.581	0.495	0.703	0.656	0.879	0.565
14 2-Phenylethanol	0.470	0.560	0.525	0.531	0.618	0.687	0.801	0.603

parameters influence  $\rho$  values. With single solvent parameters the correlation was extremely poor. Several multiple correlations were attempted of which most were significant at well above the 99% confidence level. The typical correlation equation generated at 30 °C for

TABLE 5

Hammett polar susceptibility constants  $\rho$  for the reactions of 4-substituted 1-naphthoic acids with diazodiphenylmethane in alcohols

Solvent	$\rho$ 30 °C	$\rho$ 35 °C	$\rho$ 40 °C
1 Methanol	0.82	0.77	0.62
2 Ethanol	0.90	0.75	0.60
3 Propan-1-ol	0.94	0.79	0.64
4 Propan-2-ol	1.06	1.01	0.98
5 Butan-1-ol	0.97	0.82	0.67
6 2-Methylpropan-1-ol	0.90	0.75	0.60
7 Butan-2-ol	0.97	0.82	0.67
8 2-Methylpropan-2-ol	1.15	1.00	0.85
9 Pentan-1-ol	0.98	0.83	0.68
10 Benzyl alcohol	0.75		
11 2-Methylbutan-2-ol	1.39	1.19	1.06

biphenyl-4-carboxylic acid in 11 alcohols (except cyclopentanol, 1-phenylethanol, and 2-phenylethanol) with  $R$  0.949 and  $s$  0.017 is (11) and the corresponding

$$\rho = 0.642 - 0.902 f(\epsilon) - 0.219 \sigma^* \quad (11)$$

$$(\pm 0.236) \quad (\pm 0.042)$$

equation at 30 °C for 1-naphthoic acid is (12) with  $R$  0.984 and  $s$  0.050. It is interesting to note that in these

$$\rho = 2.545 - 3.672 f(\epsilon) - 0.739 \sigma^* \quad (12)$$

$$(\pm 0.578) \quad (\pm 0.098)$$

correlations the coefficient of the dielectric term is negative. This is in harmony with the findings of Chapman *et al.*<sup>6,7,9,10</sup>

*Relative Transmission of Electronic Effects across the Biphenyl Ring System.*—In order to understand the extent of transmission of electronic effects across the biphenyl system relative to that for benzene,  $\rho_2/\rho_1$  was calculated for eight alcohols, where  $\rho_2$  and  $\rho_1$  are the reaction constants in the biphenyl and benzene systems, respectively. This calculation is based on the assumption that the  $\rho$  values are identical for the reactions of *meta*- and *para*-substituted benzoic acids in a solvent at a given temperature. For eight solvents (Table 6)

TABLE 6

Hammett polar susceptibility constants for the reactions of 4'-substituted biphenyl-4-carboxylic acids and *m*-substituted benzoic acids with diazodiphenylmethane in various solvents at 30 °C

Solvent	$\rho_2$	$\rho_1$	$\rho_2/\rho_1$
1 Methanol	0.23	0.88	0.26
2 Ethanol	0.24	0.94	0.25
3 Propan-1-ol	0.25	0.99	0.26
4 Propan-2-ol	0.28	1.07	0.26
5 Butan-1-ol	0.25		
6 2-Methylpropan-1-ol	0.25	0.94	0.27
7 Butan-2-ol	0.25		
8 2-Methylpropan-2-ol	0.34	1.28	0.27
9 Pentan-1-ol	0.25		
10 Benzyl alcohol	0.20	0.78	0.26
11 2-Methylbutan-2-ol	0.37	1.41	0.26

the ratio has the value  $0.26 \pm 0.01$ . This value closely agrees with a calculated value of 0.29, based on the Kirkwood-Westheimer theory,<sup>28</sup> estimated from the ratio of the square of the distance between the *para*-carbon atom and the carboxy carbon atom of benzoic acid to that of the corresponding distance in biphenyl-4-carboxylic acid.<sup>29</sup> This means that in all these solvents approximately a fourth of the electronic effect of a substituent in the *meta*- or *para*-position of benzoic acid is transmitted to the carboxy-group by a 4'-substituent in biphenyl-4-carboxylic acid. This result agrees with the earlier conclusion that the transmission of electronic effects in biphenyl is less than that in system and the relative transmission ranged between one-third and one-fifth.<sup>30-32</sup>

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