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Note

The reactivity of 4′-substituted-biphenyl-2-carboxylic acids with diazodiphenylmethane in various alcohols

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The reactivities of a series of 4′-substituted-biphenyl-2-carboxylic acids have been investigated in their reaction with diazodiphenylmethane, in ten alcohols at 30°C, by the known spectrophotometeric method. The rate data for these acids have been correlated with a simple Hammett equation by means of the σ_p constants. The transmission of polar effects through the double bond, in terms of the transmission coefficient ρ/ρ_0, has been discussed. For the reaction of a given acid in ten various alcohols, the log k and ρ values have been correlated through multiple regression on appropriate solvent parameters. The results obtained for 4′-substituted-biphenyl-2-carboxylic acids have been compared with the results for 2-(4-phenyl-substituted)-cyclohex-1-enylcarboxylic acids and (*Z*)-4-substituted cinnamic acids under the same experimental conditions.

In continuation of our study on the transmission of substituent effects through the double bond, we now report in this paper an extension of our previous work[1-5] on the reactivity of α,β-unsaturated carboxylic acids with diazodiphenylmethane (DDM) in various alcohols. This reaction has already been used to investigate the transmission of substituent effects through three types of double bonds, an open chain, in a ring and delocalized double bonds, in (*Z*)-4-substituted cinnamic acids[6,7] 2-(4-phenylsubstituted)-cyclohex-1-enylcarboxylic acids[6] and 4′-substituted-biphenyl-2-carboxylic acids[6,8], respectively.

In the present investigations we determined the second order rate coefficients for the esterification of the 4′-substituted-biphenyl-2-carboxylic acids with DDM in ten different alcohols. The log k and ρ values were correlated through multiple regression on appropriate solvent parameters: The Kirkwood function[9] of the relative permittivity, $f(\varepsilon_r)=(\varepsilon_r-1)/(2\varepsilon_r+1)$, Taft polar substituent constants σ^*[10] for the alkyl group of the alcohol and the number of γ-hydrogen atoms in the alcohol $n_{\gamma H}$.

The results obtained for 4′-substituted-biphenyl-2-carboxylic acids were compared with the results for 2-(4-phenylsubstituted)-cyclohex-1-enylcarboxylic acids[4] and (*Z*)-4-substituted cinnamic acids[5] previously determined under the same experimental conditions.

Values of second-order rate coefficients for the reaction of 4′-substituted-biphenyl-2-carboxylic acids with DDM in various alcohols at 30°C are given in Table I. The results obtained show that the rate constants increased with increasing polarity of the solvent. This is in accordance with the proposed mechanism of the reaction[11-13].

Solvent parameters are shown in Table II. Multiple linear regression of log k for 2-biphenylcarboxylic acid with $f(\varepsilon_r)$, σ^* and $n_{\gamma H}$ gives eqn. (1) with the multiple correlation coefficient R=0.9843 and the standard deviation of the estimate=0.107.

$$\log k = -1.435 + 5.388 f(\varepsilon_r) + 2.783\sigma^* + 0.018 n_{\gamma H} \quad \ldots (1)$$
$$(\pm 1.064) \quad (\pm 0.165) \quad (\pm 0.010)$$

The corresponding expressions for 2-phenylcyclohex-1-enylcarboxylic acid and for *Z*-cinnamic acid reacting with DDM in the same series of alcohols are eqn. (2) with R=0.9915 and s=0.078 and eqn. (3) with R=0.9891 and s=0.073.

$$\log k = 1.825 + 4.856 f(\varepsilon_r) + 2.854\sigma^* + 0.026 n_{\gamma H} \quad \ldots (2)$$
$$(\pm 1.059) \quad (\pm 0.190) \quad (\pm 0.013)$$

$$\log k = 1.192 + 4.076 f(\varepsilon_r) + 2.352\sigma^* + 0.022 n_{\gamma H} \quad \ldots (3)$$
$$(\pm 0.992) \quad (\pm 0.178) \quad (\pm 0.012)$$

Regression analysis in the work was carried out with the ICL Statistical Analysis Package Mark 2XDS3. All the above correlations are significant between 99% and 99.9% confidence limits.

Equations (1), (2) and (3) show that the 2-biphenylcarboxylic acid system is slightly sensitive to solvent polarity changes that the 2-phenylcyclohex-1-enylcarboxylic and *Z*-cinnamic acid system. This is confirmed by the larger coefficient of $f(\varepsilon_r)$, in eqn. (1).

Table I—Rate coefficients ($dm^3\ mol^{-1}\ min^{-1}$) for the reaction of 4′-substituted-biphenyl-2-carboxylic acids with diazodiphenylmethane in various alcohols at 30°C

Solvent	Substituent							ε_r[a]
	H	CH_3	OCH_3	Cl	Br	I	NO_2	
Methanol	11.61	10.68	9.56	13.52	13.88	14.26	22.07	32.70
Ethanol	5.00	4.26	3.99	5.87	6.12	6.34	9.55	24.55
Propan-1-ol	5.52	4.78	4.54	6.48	6.60	6.92	10.89	20.33
Propan-2-ol	4.68	3.98	3.72	5.42	5.71	6.04	9.14	19.41
2-Methylpropan-1-ol	6.82	6.18	5.64	7.99	8.26	8.78	13.80	17.93
Butan-1-ol	4.26	3.88	3.54	5.26	5.61	5.93	8.84	17.51
Butan-2-ol	3.84	3.52	3.18	4.70	5.08	5.25	8.06	16.56
Benzyl alcohol	42.03	37.46	34.90	51.45	54.88	58.11	86.08	12.80
2-Methylpropan-2-ol	1.40	1.26	1.06	1.84	2.26	2.68	3.76	12.47
2-Methylbutan-2-ol	0.56	0.52	0.43	0.80	0.94	1.26	1.96	5.82

[a] Relative permittivity at 30° (ref. 14)

Table II—Solvent parameters for alcohols

Solvent	ε_r[a]	σ^*[b]	$n_{\gamma H}$[c]
Methanol	32.70	−0.10	0
Ethanol	24.55	−0.115	0
Propan-1-ol	20.33	−0.19	3
Propan-2-ol	19.41	−0.125	0
2-Methylpropan-1-ol	17.93	−0.13	6
Butan-1-ol	17.51	−0.21	2
Butan-2-ol	16.56	−0.21	3
Benzyl alcohol	12.80	+0.215	0
2-Methylpropan-2-ol	12.47	−0.30	0
2-Methylbutan-2-ol	5.82	−0.31	3

[a] Relative permittivity at 30°C (ref. 17)
[b] Taft polar substituent constants of the alkyl groups (ref. 10)
[c] Number of γ-hydrogen atoms in the alcohol

Table III—Hammett reaction constants for the reactivity of th 4′-substituted-biphenyl-2-carboxylic acids

Solvent	ρ	r[a]
Methanol	0.334	0.9813
Ethanol	0.364	0.9912
Propan-1-ol	0.366	0.9925
Propan-2-ol	0.376	0.9881
2-Methylpropan-1-ol	0.367	0.9886
Butan-1-ol	0.384	0.9830
Butan-2-ol	0.388	0.9860
Benzyl alcohol	0.383	0.9830
2-Methylpropan-2-ol	0.532	0.9378
2-Methylbutan-2-ol	0.638	0.9413

[a] Correlation coefficient
Number of substituents studied, n=7

The data from Table I have been correlated with the simple Hammett equation by means of σ_p constants[15]. Satisfactory correlations have been obtained and are shown in Table III.

The ratio ρ/ρ_0 was used to evaluate the transmission of electronic effects by relevant groups, where ρ_0 is the reaction constant of the reference system (*p*-substituted benzoic acids)[12] at the same temperature and in the same solvent. These ratios are given in Table IV.

Starting from the assumption of similarity in the transmitting cavities for 4′-substituted-biphenyl-2-carboxylic acids, 2-(4-phenylsubstituted)-cyclohex-1-enylcarboxylic acids and *Z*-4-substituted cinnamic acids we consider that the differences in the transmission coefficients (ρ/ρ_0

Table IV—Ratio of reaction constants ρ/ρ_0

Solvent	4′-substituted-biphenyl-2-carboxylic acids	2-(4-phenyl substituted) -cyclohex-1-enyl carboxylic acids	*Z*-4-substituted cinnamic acids
Methanol	0.377	0.610	0.651
Ethanol	0.385	0.631	0.679
Propan-1-ol	0.369	0.625	0.697
Propan-2-ol	0.353	0.594	0.657
2-Methyl-propan-1-ol	0.392	0.645	0.732
Benzyl alcohol	0.492	0.823	0.883
2-Methyl-propan-2-ol	0.416	0.602	0.671
2-Methyl-butan-2-ol	0.451	0.595	0.630

ca. 0.404, 0.640 and 0.700 respectively) cannot be ascribed only to the differences in the polarizability of the investigated double bonds.

The results given in Table III show that the ρ values are described by increasing relative permittivity. This may be interpreted in two ways. Firstly, the transmission of the polar effects of the substituents through the medium increases in importance relative to transmission through the molecular cavity as ε_r is decreased. Secondly, at high relative permittivities the energy necessary to bring about the charge separation in the transition state is relatively small and this gives rise to a low susceptibility to the polar effects of substituents. The ρ value thus increases as the energy necessary to achieve the charge separation increases as ε_r is decreased. It is thus reasonable to correlate ρ with $f(\varepsilon_r)$, σ* and $n_{\gamma H}$ as for log *k*.

For 4′-substituted-biphenyl-2-carboxylic acids eqn. (4) holds

$$\rho_1 = 1.723 - 2.930 f(\varepsilon_r) - 0.203\sigma^* - 0.008 n_{\gamma H} \quad \ldots (4)$$
$$(\pm 0.322) \quad (\pm 0.078) \quad (\pm 0.003)$$

with R=0.9782 and s=0.024, for 2-(4-phenyl-substituted)-cyclohex-1-enylcarboxylic acids eqn. (5) with R=0.9644 and s=0.028 and for *Z*-4-substituted cinnamic acids eqn. (6) with R=0.9120 and s=0.047.

$$\rho_2 = 1.825 - 2.625 f(\varepsilon_r) - 0.198\sigma^* - 0.007 n_{\gamma H} \quad \ldots (5)$$
$$(\pm 0.384) \quad (\pm 0.069) \quad (\pm 0.004)$$

$$\rho_3 = 1.723 - 2.286 f(\varepsilon_r) - 0.283\sigma^* - 0.003 n_{\gamma H} \quad \ldots (6)$$
$$(\pm 0.645) \quad (\pm 0.116) \quad (\pm 0.001)$$

A comparison of eqns (4), (5) and (6) shows that the 4′-substituted-biphenyl-2-carboxylic acids is slightly sensitive to solvent polarity changes than 2- (4-phenylsubstituted)-cyclohex-1-enyl-carboxylic acids and *Z*-4-substituted cinnamic acids. These results are completely in agreement with the structural and stereochemical characteristics of the investigated acids and agrees with our previous studies of steric hindrance of the resonance effect[6,19,20].

Experimental Section

Materials. Biphenyl-2-carboxylic acid was commercially available (Fluka).

4′-Substituted-biphenyl-2-carboxylic acids. 4′-Methyl, -methoxy, -chloro, -bromo, -iodo and -nitro derivatives were prepared by previously reported methods[16–18]. The compounds had m.ps in good agreement with literature values.

The solvents and DDM were prepared as described previously[5].

Kinetic measurements. The rate coefficients for the reaction of biphenyl-2-carboxylic acid and 4′-substituted-biphenyl-2-carboxylic acids with DDM were determined by the known spectrophotometric method as described previously[4].

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