The Effects of Substituents on the Rate of Saponification of Biphenyl-4-carboxylates

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Second-order rate constants have been measured for the saponification of methyl 2′-, 3′-, and 4′-substituted biphenyl-4-carboxylates at several temperatures in 85% (w/w) methanol–water and activation parameters have been calculated. The Hammett equation applies very well to the saponification of 3′- and 4′-substituted biphenyl-4-carboxylates with σ-constants evaluated by the FMMF method. The effect of 2′-substituents is understandable in terms of π-electron steric effects.

Although extensive studies have been made to correlate the reactivities of *meta*- and *para*-substituted benzene derivatives in a large number of reactions,[1] relatively very few studies have been made in this direction for derivatives of biphenyl and many other polynuclear hydrocarbons. In continuation of our studies of the effect of substituents in the biphenyl system,[2] we have now investigated the kinetics of saponification of several methyl 2′-, 3′-, and 4′-substituted biphenyl-4-carboxylates.

Experimental

Materials.—All the esters used were prepared from the corresponding biphenyl-4-carboxylic acids,[3] by heating them in methanol containing a few drops of concentrated sulphuric acid under reflux for 6 h. Table 1 lists the new compounds, their m.p.s, and analyses. Methanol was purified by the method of Lund and Bjerrum.[4] Triply distilled water was used for dilution.

Rate Measurements.—The solvent used was 85% (w/w) methanol–water. The temperature was controlled to ±0.1 °C. The reactions were studied under second-order conditions and followed by the methods described earlier.[5] At 50 °C aliquot portions were sealed in ampoules and analysed at intervals.

Results and Discussion

The kinetic results are shown in Table 2. The rate constants given are the average of those obtained from at least three independent determinations for each compound. The data indicate that electron-withdrawing groups increase and electron-donating groups decrease the rate.

Activation Parameters.—The activation energies were computed from the linear plots of log k against $1/T$. The values of the activation energies show a regular variation with substituents: electron-withdrawing groups decrease and electron-donating groups increase E_a. The entropies of activation are negative as for bimolecular reactions.

Linear Free Energy Relationships.—With a view to seeking a Hammett correlation,[6] we converted Byron *et al.*'s [7] pK_a values for 3′- and 4′-substituted biphenyl-4-carboxylic acids into σ_{ij} values by dividing the ΔpK_a values by a ρ value of 1.32 based on benzoic acid ionization in 50% 2-n-butoxyethanol–water.[8] The Hammett correlation with these values was very poor (r 0.884 at 30 °C). Similar poor correlations were observed at 40 and 50 °C. The reason for the poor correlation may be due to the approximate nature of the pK_a values of Byron *et al.*, which generated two separate lines for 3′- and 4′-substituted biphenyl-4-carboxylic acids when plotted against ordinary Hammett σ-constants. The point for the 4′-cyano-group shows considerable deviation. This is

Table 1. Methyl biphenyl-4-carboxylates

Substituent	M.p. (°C)	Recrystallisation solvent	Found (%)		Formula	Required (%)	
			C	H		C	H
3′-F	104—106	A	73.1	4.8	$C_{14}H_{11}FO_2$	73.0	4.8
3′-Br	138—139	B	57.8	3.8	$C_{14}H_{11}BrO_2$	57.7	3.8
3′-CN	107—108	C	75.9	4.8	$C_{15}H_{11}NO_2$	75.9	4.6
3′-NO$_2$	145—147	B	65.5	4.4	$C_{14}H_{11}NO_4$	65.4	4.3
3′-CH$_3$	114—115	C	79.8	6.3	$C_{15}H_{14}O_2$	79.6	6.2
3′-OCH$_3$	128—129	B	74.4	5.9	$C_{15}H_{14}O_3$	74.4	5.8
4′-F	133—135	A	73.1	4.9	$C_{14}H_{11}FO_2$	73.0	4.8
4′-CN	102—103	A	75.9	4.7	$C_{15}H_{11}NO_2$	75.9	4.6
2′-F	110—111	A	73.1	4.9	$C_{14}H_{11}FO_2$	73.0	4.8
2′-Cl	97—98	C	68.1	4.6	$C_{14}H_{11}ClO_2$	68.2	4.5
2′-Br	115—116	D	57.9	3.9	$C_{14}H_{11}BrO_2$	57.7	3.8
2′-CN	117—118	D	76.0	4.7	$C_{15}H_{11}NO_2$	75.9	4.6
2′-CH$_3$	77—78	E	79.7	6.2	$C_{15}H_{14}O_2$	79.6	6.2
2′-OCH$_3$	85—86	C	74.5	5.8	$C_{15}H_{14}O_3$	74.4	5.8

A, Methanol; B, benzene; C, ethanol; D, ligroin; E, light petroleum.

Table 2. Second-order rate constants and activation parameters for the saponification of methyl substituted biphenyl-4-carboxylates in 85% (w/w) methanol–water

No.	Substituent	10^4k/l mol^{-1} s^{-1} 30 °C	40 °C	50 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}	log A/s^{-1}
1	H	2.59 ± 0.09	7.81 ± 0.01	16.39 ± 0.19	17.3 ± 0.2	17.7 ± 0.1	9.4
2	3′-F	4.02 ± 0.06	11.52 ± 0.08	23.25 ± 0.18	16.5 ± 0.1	19.6 ± 0.2	9.1
3	3′-Cl	4.10 ± 0.07	12.04 ± 0.06	24.10 ± 0.09	16.7 ± 0.1	19.1 ± 0.2	9.1
4	3′-Br	4.23 ± 0.09	12.19 ± 0.05	24.59 ± 0.08	16.6 ± 0.1	19.1 ± 0.2	9.1
5	3′-CN	5.21 ± 0.09	14.91 ± 0.08	29.19 ± 0.08	16.2 ± 0.1	20.1 ± 0.1	8.9
6	3′-NO_2	6.33 ± 0.07	17.79 ± 0.08	34.19 ± 0.19	15.9 ± 0.2	20.8 ± 0.1	8.7
7	3′-CH_3	2.41 ± 0.03	7.19 ± 0.02	15.29 ± 0.01	17.4 ± 0.2	17.5 ± 0.1	9.4
8	3′-OCH_3	2.71 ± 0.09	8.11 ± 0.01	17.01 ± 0.09	17.5 ± 0.2	17.1 ± 0.1	9.5
9	4′-F	2.81 ± 0.09	8.41 ± 0.09	17.49 ± 0.21	17.2 ± 0.1	17.9 ± 0.1	9.4
10	4′-Cl	3.41 ± 0.09	10.51 ± 0.08	20.89 ± 0.49	17.1 ± 0.2	18.0 ± 0.2	9.3
11	4′-Br	3.51 ± 0.09	10.69 ± 0.01	21.29 ± 0.49	16.9 ± 0.2	18.6 ± 0.2	9.2
12	4′-CN	5.90 ± 0.10	16.71 ± 0.11	32.51 ± 0.11	16.2 ± 0.2	19.6 ± 0.1	9.0
13	4′-NO_2	6.81 ± 0.11	20.01 ± 0.12	38.11 ± 0.21	16.0 ± 0.1	20.4 ± 0.1	8.8
14	4′-CH_3	2.11 ± 0.11	6.31 ± 0.01	13.71 ± 0.21	18.9 ± 0.1	13.5 ± 0.1	10.3
15	4′-OCH_3	1.82 ± 0.06	5.70 ± 0.02	12.41 ± 0.11	20.1 ± 0.1	9.0 ± 0.1	11.3
16	2′-F	2.40 ± 0.01	7.51 ± 0.05	15.91 ± 0.11	17.4 ± 0.2	18.0 ± 0.1	9.3
17	2′-Cl	2.21 ± 0.02	7.20 ± 0.02	15.41 ± 0.11	17.2 ± 0.1	17.6 ± 0.1	9.4
18	2′-Br	2.09 ± 0.03	7.02 ± 0.05	15.15 ± 0.05	17.3 ± 0.1	17.6 ± 0.2	9.2
19	2′-CN	1.81 ± 0.03	5.01 ± 0.02	11.01 ± 0.03	20.0 ± 0.2	10.0 ± 0.1	11.1
20	2′-NO_2	3.20 ± 0.02	8.24 ± 0.04	17.41 ± 0.11	17.0 ± 0.1	18.2 ± 0.2	9.5
21	2′-CH_3	1.90 ± 0.03	5.80 ± 0.03	13.11 ± 0.11	20.1 ± 0.2	10.1 ± 0.1	11.0
22	2′-OCH_3	1.51 ± 0.02	4.11 ± 0.02	10.10 ± 0.09	20.8 ± 0.1	9.8 ± 0.1	11.2

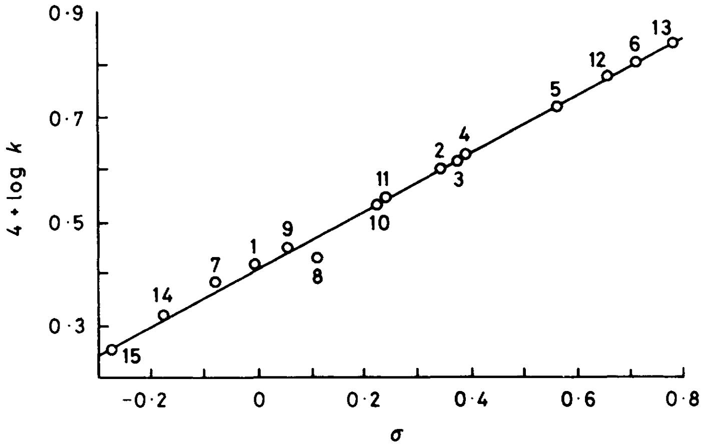

Figure. Plot of σ values against log k. For key see Table 2

understandable because the 4′-cyanobiphenyl-4-carboxylic acid prepared by Byron *et al.* was impure and consequently the pK_a value of the acid must be approximate. However, a plot of log k at 30 °C for methyl 3′- and 4′-substituted biphenyl-4-carboxylates against ordinary Hammett σ_m and σ_p values based on benzoic acid ionization in water shows an excellent correlation (Figure) with ρ 0.546 (r 0.999, s 0.016), only the point for 3′-OMe deviating a little. The σ value used by us for 3′-OMe is 0.115 which is same as σ_m for this group. Similar good correlations exist at higher temperatures (ρ 0.50, r 0.997 and 40 °C and ρ 0.46, r 0.996 at 50 °C). These low values of ρ, according to the significance generally attached to them, seem to indicate that the substituent effect is not pronounced in this reaction. The effective σ value for *m*-OMe in our system appears to be *ca.* 0.04. Aslam *et al.*[9] found values for σ_m for OMe in non-aqueous media of *ca.* +0.02—+0.05. As the solvent used by us, 85% (w/w) methanol–water, is sufficiently non-aqueous, a σ value of +0.04 observed for *m*-OMe is quite acceptable.

The good linear relationship in the Figure indicates that the additional benzene ring in biphenyl does not affect the composition of the electrical effect which reaches the reaction centre, *i.e.* the relative importance of inductive and resonance effect is unchanged. This may also show that any effect that was responsible for generating two separate lines for the 3′- and 4′-substituents with Byron *et al.*'s data does not seem to operate in biphenyl.

Since the correlation was poor with σ_{ij} values derived from the ionization constants of 3′- and 4′-substituted biphenyl-4-carboxylic acids,[7] correlation was attempted with σ_{ij} values based on the Dewar–Golden–Harris (DGH) treatment.[10] The log k values at 30 °C give an excellent correlation (r 0.993), ρ 1.46, providing interesting confirmation that the DGH treatment is fairly successful for biphenyl. This treatment gives ρ values of 1.37 (r 0.995) and 1.22 (r 0.994) at 40 and 50 °C, respectively.

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, the ratio of the ρ value of 0.55 obtained for the saponification of methyl 3′- and 4′-substituted biphenyl-4-carboxylates to that of 2.23 obtained by Baliah and Ananthakrishnanadar [5] at 30 °C in the same solvent for the saponification of methyl *meta*- and *para*-substituted benzoates has been calculated. This ratio of 0.25 agrees with a value of 0.29 calculated based on the Kirkwood–Westheimer theory,[11] 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.[10] This means that approximately a fourth of the electronic effect of a substituent in the *meta*- or *para*-position of a benzene derivative is transmitted from the 3′- or 4′-position of biphenyl to its 4-position. This agrees with our earlier observation.[2]

The Effect of 2′-Substituents.—The data in Table 2 show that the Hammett equation is not applicable to the reactivity of methyl 2′-substituted biphenyl-4-carboxylates. All the 2′-substituents (except NO_2) decrease the rate of the parent. This cannot be explained by the internally transmitted electronic effects of the substituents. When the 2′-substituents, irrespective of their electronic nature, impose strain upon the system, this will result in diminished conjugation between the 2′- and 4′-positions as a result of the two rings becoming nearly perpendicular. The rate behaviour indicates that a substituent relays more electrons to the reaction centre from the 2′-position than it does from the 3′- or 4′-position. This may be caused by a physical displacement of the π-electron by the substituents from the ring carrying the reaction centre arising from the close proximity of the 2′-substituents to the π-electrons. This effect has been referred to as π-electron steric effect.[7,12] That the compressional effect on the π-electron plays a decisive role is seen from the progressive decrease in rate as the size of the 2′-halogeno-substituents increases.

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