

Substituent Effects on the Formation Constants of Substituted Acetophenone-Iodine Complexes

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The formation constants of complexes of iodine with 11 *meta*- and *para*-substituted acetophenones are reported for heptane solutions at 25° and correlated by various linear free energy relationships. Neither σ , σ^+ , or a combination of σ^0 (or σ^{an}) and σ^+ satisfactorily correlate the data. Dual substituent parameter equations furnish better results and show that the effects of *meta*-substituents are not of the σ^0 type whilst those of *para*-substituents are of the σ_{R}^+ type. The Thirot equation gives the best empirical fit to the data.

In a recent publication,¹ the difficulties encountered in distinguishing between neighbouring formation constants of complexes were solved by directly comparing their values. The tests carried out on iodine complexes with various carbonyl compounds have shown that this method can be applied when the ratio of the constants is near unity and the electron donors have similar structures. Substituted acetophenones meet these conditions, and the values of the $K : K_0$ ratios, where K_0 is the constant for acetophenone and K those for the substituted compounds have thus been determined. Previously Foster and Goldstein,² using the Ketelaar method, determined K for some aryl ketone-iodine complexes and noted that the Hammett equation held for equilibrium constants of formation of four *para*-substituted acetophenone-iodine complexes. The accuracy gained by employing our method is demonstrated by the ± 0.03 and ± 0.02 errors (95% confidence level) compared with the probable errors (50% confidence level) ± 0.14 for $K_{p\text{-OH}_3} : K_0$ and ± 0.15 for $K_{p\text{-Cl}} : K_0$ quoted by Foster and Goldstein when standard procedures were employed. Because we have more numerous and accurate data, the applicability of linear free energy relationships to the formation equilibrium of substituted acetophenone-iodine complexes may be more thoroughly discussed.

RESULTS

Equilibrium constants and corresponding free energy variations are shown in Table 1. Fits of $\log K : K_0$ by a least-square treatment to Hammett, Brown, different dual-substituent parameter, and Thirot equations are given in Tables 2–4. Standard deviations, correlation coefficients, and following Taft's suggestion,³ the quantity standard deviation/root mean square $\equiv f$, were calculated. Experience has shown that correlations of good precision are those with $f \leq 0.1$.

DISCUSSION

The Hammett, Brown, and Yukawa-Tsuno Equations.—The Hammett equation (1) is not considered satisfactory as $f = 0.36$. In particular electron attraction by *m*-CF₃ is stronger than *p*-CF₃, while $\sigma_{p\text{-CF}_3}$ is greater than

$$\log K/K_0 = -0.58\sigma_{m,p} + 0.025 \quad (1)$$

$\sigma_{m\text{-CF}_3}$. Similarly *m*-OMe becomes electron repelling

¹ M. H. Ducoin, G. Guihéneuf, and B. Wojtkowiak, *J. Chim. phys.*, 1974, **71**, 448.

² J. Foster and M. Goldstein, *Spectrochim. Acta*, 1968, **7A**, 807.

³ S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 3.

while its σ_m value is positive, and *p*-F has an effect almost identical with that of hydrogen even though its value is significantly different from zero.

TABLE 1

Thermodynamic data for substituted acetophenone-iodine complexes in n-heptane at 25°

Substituent	K/K_0 ^a	$K/1 \text{ mol}^{-1}$ ^d	$\delta\Delta G/\text{cal mol}^{-1}$ ^e
<i>p</i> -OMe	1.69 ± 0.08	1.94	311 ± 30
<i>p</i> -Me	1.25 ± 0.03 ^b	1.44	132 ± 14
<i>p</i> -F	0.81 ± 0.015	0.93	-125 ± 11
<i>p</i> -Cl	0.75 ± 0.02 ^c	0.82	-170 ± 16
<i>p</i> -CF ₃	0.57 ± 0.015	0.66	-333 ± 16
H	1	1.15	0
<i>m</i> -OMe	1.19 ± 0.03	1.37	103 ± 15
<i>m</i> -Me	1.12 ± 0.02	1.29	67 ± 11
<i>m</i> -Cl	0.64 ± 0.02	0.74	-264 ± 19
<i>m</i> -Br	0.66 ± 0.02	0.76	-246 ± 18
<i>m</i> -CF ₃	0.50 ± 0.02	0.58	-410 ± 25

^a Determined by the direct comparison of constants. The reproducibility is given at the 95% confidence level usually obtained. ^b Foster's value 1.23 ± 0.14 . ^c Foster's value 0.58 ± 0.15 . ^d Absolute values calculated from the K/K_0 ratio and K_0 1.15 ± 0.04 1 mol^{-1} determined by Rose and Drago's method (N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 1959, **81**, 6138). ^e $\delta\Delta G = -298 R \log(K/K_0)$.

TABLE 2

Fit of $\log K/K_0$ to the Hammett and Brown equations

Substituent constant	ρ^a	Standard deviation	Correlation coefficient	f
σ_m	-0.64	0.072	0.908	0.43
σ_p	-0.56	0.054	0.959	0.35
$\sigma_{m,p}$	-0.58	0.061	0.936	0.36
σ_m^+	-0.59	0.046	0.963	0.27
σ_p^+	-0.35	0.050	0.964	0.32
$\sigma_{m,p}^+$	-0.38	0.065	0.927	0.38

^a Susceptibility of the equilibrium to substituent effects; number of points $n = 6$.

If the Hammett σ is replaced by the Brown $\sigma_{m,p}^+$ factor ⁴ which is better adapted to $+R$ functional groups (*i.e.* the acetyl group), the value of f (0.38) is even worse. In fact it is desirable to examine the *para*- and *meta*-series separately, as Hine ⁵ demonstrated theoretically and Laurence and Berthelot ⁶ confirmed experimentally for the relationship between $\nu(\text{CO})$ for acetophenones and σ^+ . This process gives significantly different coefficients (ρ_m 0.59, ρ_p -0.35) at a confidence level ranging from

⁴ O. Exner, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, p. 2.

⁵ J. Hine, *J. Amer. Chem. Soc.*, 1959, **81**, 1126.

⁶ M. Berthelot and C. Laurence, *Canad. J. Chem.*, in the press.

95 to 98%* and more satisfactory values of f (f_m 0.27 f_p 0.32). The unusual behaviour of the points m - and p -CF₃ can thus be explained by the fact that $\log K/K_0$ is more sensitive to the effect of *meta*-substituents.

For the *para*-series, the Yukawa-Tsuno relationship⁴ (2) may also be applied either with the Taft σ^0 factor⁴ or

$$\log K/K_0 = \rho[\sigma_p^0 + r(\sigma_p^+ - \sigma_p^0)] \quad (2)$$

the Wepster σ^n factor.⁷ Consequently the f values are better † though they are still far from the limit recommended by Taft.

Dual Substituent Parameter Equations.—These may be

is that its attracting inductive effect overcomes its repelling π delocalisation effect.

para-Substituent Effects.—Only the Taft σ_R^+ parameter, which gives f 0.15, comes near the limit of a good correlation. For the other parameters f ranges from 0.32 to 0.40. The equilibria investigated obviously belong to the σ_R^+ type, which corresponds to greater polarisation of the carbonyl group in the complex than in the free state. The increasing π electron demand at the reaction centre thus explains the unusual behaviour of the p -F substituent in which the repelling π -delocalisation effect almost completely cancels the attracting inductive effect.

TABLE 3
Fit of $\log K/K_0$ to various dual substituent parameter equations^a

Parameters		ρ_I ^b	ρ_R ^c	P_R ^d	Standard deviation	Correlation coefficient	
σ_I, σ_R^0	m	-0.59	-0.50	46	0.025	0.992	0.15
	p	-0.57	-0.66	54	0.060	0.961	0.39
$\sigma_I, \sigma_{R(BA)}$	m	-0.58	-0.39	40	0.010	0.999	0.06
	p	-0.58	-0.52	47	0.049	0.974	0.32
σ_I, σ_R^+	m	-0.56	-0.24	30	0.017	0.996	0.10
	p	-0.53	-0.34	39	0.023	0.995	0.15
σ_I', σ_R'	m	-0.64	-0.46	42	0.014	0.997	0.08
	p	-0.67	-0.56	46	0.063	0.958	0.41
\mathcal{F}, \mathcal{R}	m	-0.34	-0.44	56	0.016	0.997	0.10
	p	-0.32	-0.55	63	0.062	0.959	0.40
$\sigma^0, \Delta\sigma^+$ ^e	p	-0.46 ^g	-0.23 ^h		0.044	0.979	0.28
	$\sigma^n, \Delta\sigma^+$ ^f	p	-0.50 ^g		0.040	0.983	0.26

^a $n = 6$. ^b Sensitivity of the equilibrium to inductive effects. ^c Sensitivity of the equilibrium to π delocalisation effects. ^d Percentage π delocalisation. ^e $\Delta\sigma^+ = \sigma_p^+ - \sigma_p^0$. ^f $\Delta\sigma^+ = \sigma_p - \sigma_p^0$. ^g ρ In the Yukawa-Tsuno equation. ^h ρ_r .

TABLE 4
Fit of $\log K/K_0$ to the Thirost equation^a

Parameters		ρ_I	ρ_{R_1} ^b	ρ_{R_2} ^c	Standard deviation	Correlation coefficient	
$\sigma^H, \Delta\sigma_1$	m	-0.13	0.10		0.024	0.993	0.14
$\sigma^H, \Delta\sigma_1, \Delta\sigma_2$	p	-0.092	0.076	0.078	0.016	0.998	0.10

^a $n = 6$. ^b Sensitivity of the equilibrium to π delocalisation effects of the first type. ^c Sensitivity of the equilibrium to π delocalisation effects of the second type.

written as (3) where σ_i and σ_r may be Taft $\sigma_I, \sigma_R^0, \sigma_I, \sigma_{R(BA)}$ or σ_I, σ_R^+ factors,³ Exner σ_I', σ_R' factors,⁴ or Swain and Lupton \mathcal{F} and \mathcal{R} factors.⁴ The contribution

$$\log K/K_0 = \rho_I\sigma_i + \rho_R\sigma_r \quad (3)$$

of the electronic effect has been defined as $P_R = 100\rho_R/(\rho_I + \rho_R)$ where P_R is the percentage of delocalisation.⁸

meta-Substituent Effects.—All the parameters used give $f \leq 0.1$, except σ_R^0 which gives $f = 0.15$. In the equilibria studied, the effects of *meta*-substituents cannot be considered to be of the σ^0 type. For all the *meta*-correlations the percentage of π delocalisation (Table 3) is abnormally high in relation to that generally found for *meta*-substituents (*e.g.*, the separation of σ_m into σ_I and $\sigma_{R(BA)}$ gives P_R 25).⁸ Consequently the best explanation of the electron-repelling behaviour of the *m*-OMe group

* The difference $\rho_p - \rho_m$ is tested by calculating the value $t = (\rho_p - \rho_m)/s$ where s is the standard deviation of $\rho_p - \rho_m$. Tables of t are referred to for the corresponding degree of freedom.

† For σ^0 $f = 0.28$ and σ^n $f = 0.26$. However this is not conclusive evidence of the superiority of Wepster's values, since the substituent p -NH₂, for which σ^n and σ^0 diverge most, has not been studied.

‡ The symbols, ρ_I, ρ_{R_1} , and ρ_{R_2} used in this paper have been substituted for Thirost's ρ, r , and s .

*The Thirost Equation.*⁹—This has been applied to both *meta*- and *para*-substituents [equations (4) and (5)].

$$\log K/K_0 = \rho_I\sigma^H + \rho_{R_1}\Delta\sigma_1 \quad (4)$$

$$\log K/K_0 = \rho_I\sigma^H + \rho_{R_1}\Delta\sigma_1 + \rho_{R_2}\Delta\sigma_2 \quad (5) \ddagger$$

The Thirost parameters give a better value of the sum $f_m + f_p$ (0.24) than σ_I, σ_R^+ (0.25), $\sigma_I, \sigma_{R(BA)}$ (0.38), σ_I', σ_R' (0.49), or \mathcal{F}, \mathcal{R} (0.50). The success of the Thirost equation may be due simply to the greater number of parameters. Indeed both the number and kind of substituent data within our series are critical since the substituents NH₂ and NO₂ were not available (because of low solubility of nitro- and amino-acetophenones in heptane). Moreover the empirical definition of $\Delta\sigma_1$ and $\Delta\sigma_2$, the rather infrequent use of the equation to date,¹⁰⁻¹³

⁷ A. J. Hoefnagel and B. M. Wepster, *J. Amer. Chem. Soc.*, 1973, **95**, 5357.

⁸ M. Charton, *Progr. Phys. Org. Chem.*, 1973, **10**, 84.

⁹ G. Thirost, *Bull. Soc. chim. France*, 1967, 739.

¹⁰ G. Thirost, *Bull. Soc. chim. France*, 1967, 3559; 1968, 1989.

¹¹ C. Kirsche and C. Caillet, *Compt. rend.*, 1971, **272**, 1331.

¹² J. Mayer, C. Caillet, and G. Thirost, *Bull. Soc. chim. France*, 1971, 4129.

¹³ M. Berthelot, C. Laurence, and B. Wojtkowiak, *Bull. Soc. chim. France*, 1973, 662.

and certain restrictions observed for $-R$ substituents¹³ do not provide conclusive evidence of the generality of this new equation.

EXPERIMENTAL

Method.—The ratios of formation constants were obtained from the I_2 absorption at 550 nm and higher wavelengths by the procedure described previously.¹

Materials.—Iodine was resublimed under reduced pressure and stored in a vacuum desiccator. Acetophenones were

recrystallised several times from light petroleum (*p*-OMe), fractionally crystallised (*p*-Cl, *m*-Cl, *m*-Br), or fractionally distilled on a Podbielnak column (*p*-Me, *m*-Me, *p*-F, *p*-CF₃, *m*-CF₃, *m*-OMe, H).

Solutions.—Microburettes (5 ml) were used to prepare solutions in heptane (Merck Uvasol).

Spectra.—These were recorded on a Beckman DK 2A spectrophotometer with fused silica cells of 1.0 cm optical path, with a thermostatted cell compartment at $25 \pm 0.2^\circ$.

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