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SUBSTITUENT EFFECTS IN π-(TRICARBONYLCHROMIUM)ARENES

V *. THERMODYNAMIC DISSOCIATION CONSTANTS OF SOME SUBSTITUTED π-(TRICARBONYLCHROMIUM)BENZOIC ACIDS

F. VAN MEURS *, A.J. HOEFNAGEL, B.M. WEPSTER and H. VAN BEKKUM
Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, Delft-2208 (The Netherlands)

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Summary

The thermodynamic dissociation constants of a series of 38 substituted π-(tricarbonylchromium)benzoic acids in 50% aqueous ethanol at 25°C have been determined. The results require revision of some literature values.

The pK_a^*-values of the π-(tricarbonylchromium)benzoic acids were correlated with the electronic substituent parameters in terms of the Yukawa—Tsuno equation. The reaction constant (ρ) decreases from 1.4 for the benzoic acids to 0.8 for the π-(tricarbonylchromium)benzoic acids, reflecting the decreased ability of the complexed aromatic system to transmit electronic substituent effects. For the alkylsubstituted π-(tricarbonylchromium)benzoic acids, conformational effects of the $Cr(CO)_3$ group can account for some of the anomalies observed. The substituent parameters, σ_{meta} and σ_{para}, of the π-($Cr(CO)_3$)phenyl group as a substituent were derived from the dissociation constants of the complexed phenylbenzoic acids.

Introduction

In Part III [1] of this series the substituent effects on the IR spectra of some substituted methyl π-(tricarbonylchromium)benzoates were reported. The correlation between the metal carbonyl stretching force constants and Hammett substituent parameters was satisfactory. On the other hand, the relationship between these substituent parameters and the ester carbonyl stretching frequencies for the methyl π-(tricarbonylchromium)benzoates was rather poor. Conformational influences of the $Cr(CO)_3$ group might account for some of the anomalies observed. This is further supported by ^1H NMR results on the substi-

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* For parts III and IV see refs. 1 and 2, respectively.

tuted methyl π-(tricarbonylchromium)benzoates [2].

As early as 1958, Fischer et al. [3] and Nicholls and Whiting [4] noted the electron-withdrawing character of the $Cr(CO)_3$ group when coordinated to an arene ring, e.g. by showing the acid strength of benzoic acid in aqueous ethanol to be increased by 0.9 p*K*-unit upon complexation with the $Cr(CO)_3$ moiety. Recently, the pK_a^*-values of a series of seven alkylsubstituted π-(tricarbonylchromium)benzoic acids were reported by Ashraf and Jackson [5]. Some doubts about their results led us to reinvestigate the dissociation of an extended series of complexed benzoic acids, including complexes with alkyl substituents of different bulkiness and also with substituents which differ as to their electronic effect. pK_a^*-values were determined in 50% aqueous ethanol at 25°C. The values obtained were compared with those of the free benzoic acids.

Experimental

The preparation of the substituted methyl π-(tricarbonylchromium)benzoates is reported in Part III [1]. Solvents were Baker Analysed reagents; they were freed from oxygen by repeated degassing and saturation with nitrogen. All preparative work was carried out under nitrogen.

Preparation of the substituted π-(tricarbonylchromium)benzoic acids

The acids (except 2,4,6-trimethyl-π-(tricarbonylchromium)benzoic acid) were prepared by hydrolysis of 1 mmol of the ester using 20 mmol KOH in 90% (v/v) aqueous methanol. If the solubility of the ester in methanol was insufficient 90% (v/v) aqueous acetone was used as the solvent. This solution was stirred at room temperature in the dark. The reaction was followed by TLC. Upon complete conversion of the ester, the solvent was removed by distillation in vacuo. The residue was dissolved in 100 ml water. Unchanged ester was removed by extraction with diethyl ether (2 × 50 ml). The acid, which precipitated upon acidification of the alkaline solution with 2 *N* HCl and cooling to 0°C, was collected by filtration. Recrystallization from aqueous methanol yielded the complexed benzoic acid, which was washed with ice-cold water and dried in vacuo. Yields were essentially quantitative. Analytical data and decomposition ranges are given in Table 1.

Preparation of 1-bromo-2,4,6-trimethyl-π-(tricarbonylchromium)benzene

This complex was prepared from 1-bromo-2,4,6-trimethylbenzene [6] and hexacarbonylchromium as described in Part III [1] using the apparatus designed by Strohmeier [7]. Recrystallization from petroleum ether (b.p. 40—60°C) yielded 35% 1-bromo-2,4,6-trimethyl-π-(tricarbonylchromium)benzene, m.p. 105—107°C (elemental analysis: found: C, 43.6; H, 3.5. $C_{12}H_{11}BrCrO_3$ calcd.: C, 43.00; H, 3.31%).

Preparation of 2,4,6-trimethyl-π-(tricarbonylchromium)benzoic acid

To a stirred solution of 600 mg (1.8 mmol) 1-bromo-2,4,6-trimethyl-π-(tricarbonylchromium)benzene in 40 ml pentane at —40°C 1.7 ml solution of n-butyllithium in hexane (2.1 *M*) was added. The temperature was raised gradually (during 3 h) to 0°C. At this temperature the suspension obtained was poured

TABLE 1

ANALYTICAL RESULTS

Substituent(s)	Decomposition point[a] (°C)	Literature decomposition point(s) (°C)	Analyses found (calcd.) (%)	
			C	H
Substituted π-(tricarbonylchromium)benzoic acids				
None	193–195	201–202 [3] 194 [4] 194–195 [5]	46.3 (46.52)	2.5 (2.34)
2-Me	152–153 [b]		48.6 (48.54)	3.0 (2.96)
2-Et	139–141		50.1 (50.35)	3.6 (3.52)
2-i-Pr	149–151		52.0 (52.00)	4.1 (4.03)
2-OMe	140–143 [b]		45.7 (45.84)	2.9 (2.80)
3-Me	151–155	150–155 [5]	48.5 (48.54)	3.1 (2.96)
3-Et	165–167		50.6 (50.35)	3.7 (3.52)
3-i-Pr	172–175	175–180 [5]	51.8 (52.00)	4.1 (4.03)
3-t-Bu	185–187		53.6 (53.50)	4.7 (4.49)
3-OMe	142–146	147–148 [10]	45.9 (48.54)	2.9 (2.80)
3-Ph	222–225		57.1 (57.49)	3.4 (3.02)
3-F	162–165	149 [11]	43.6 (43.49)	1.9 (1.83)
3-Cl	170–171		41.4 (41.04)	1.9 (1.72)
3-Br	179–185		35.9 (35.63)	1.8 (1.50)
3-COOH	228–234		44.0 (43.72)	2.3 (2.00)
3-CF_3	161–162 [b]		40.6 (40.50)	1.7 (1.55)
4-Me	148–149	149–150 [5]	48.6 (48.54)	3.1 (2.96)
4-Et	164–167	165–170 [5]	50.4 (50.35)	3.5 (3.52)
4-neoPent	205–207 [b]		55.2 (54.88)	5.2 (4.91)
4-i-Pr	153–155	153–154 [5]	51.8 (52.00)	4.1 (4.03)
4-t-Bu	172–173 [b]	172–173 [b] [5]	53.4 (53.50)	4.5 (4.49)
4-CEt_3	208–211		57.6 (57.30)	6.0 (5.66)
4-NMe_2	184–189		48.0 (47.84)	3.6 (3.68)
4-OMe	189–192		45.9 (45.84)	2.9 (2.80)
4-Ph	220–225		57.4 (57.49)	3.3 (3.02)
4-Cl	190–191		41.1 (41.04)	1.8 (1.72)
4-COOH	210–215		43.8 (43.72)	2.2 (2.00)
4-CF_3	186–188		40.6 (40.50)	1.6 (1.55)
3-(π-[$Cr(CO)_3$]Ph)	205–215		48.4 (48.52)	2.4 (2.14)
4-(π-[$Cr(CO)_3$]Ph)	215–225		48.9 (48.52)	2.5 (2.14)
2,4,6-Me_3	174–175		51.9 (52.00)	4.1 (4.03)
3,4-$(OMe)_2$	152–155		45.3 (45.29)	3.2 (3.17)
3,5-Me_2	198–203		50.5 (50.35)	3.7 (3.52)
3,5-t-Bu_2	209–215		58.2 (58.37)	6.2 (5.99)
3,5-$(OMe)_2$	190–195		45.2 (45.29)	3.3 (3.17)
3,4,5-$(OMe)_3$	172–174		44.9 (44.83)	3.6 (3.47)
Substituted benzoic acids				
3-(π-[$Cr(CO)_3$]Ph)	204–208		57.7 (57.49)	3.1 (3.02)
4-(π-[$Cr(CO)_3$]Ph)	209–214	205–210 [12]	57.7 (57.49)	3.3 (3.02)

[a] Determined on a Kofler hot plate. [b] Melting points.

onto 5 g of solid CO_2. After separation of reactants and products by extraction with 2 *N* KOH (2 × 20 ml), the alkaline layer was acidified with 2 *N* HCl and cooled. The crude acid was collected by filtration. Purification by chromatography on a light-protected silica column yielded 140 mg (26%) of lemon-yellow coloured 2,4,6-trimethyl-π-(tricarbonylchromium)benzoic acid. Analytical data are given in Table 1.

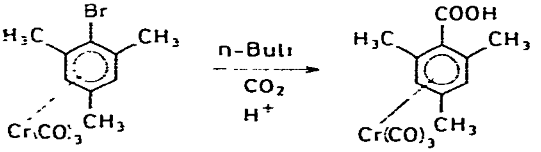
Thermodynamic dissociation constants

The solutions of the complexes were kept in the dark to prevent light-induced decomposition (cf. [8]). The molar pK_a^*-values of the substituted benzoic and π-(tricarbonylchromium)benzoic acids were calculated by means of an experimental determination of the proton activity of buffered solutions of the acids in 50% EtOH. A Beckman pH-meter type G, with glass electrodes type GP and calomel electrode type 270, was set up for measurements with the NBS phthalate buffer. The pH^* of the buffered solution in 50% (i.e. 50 volumes of absolute ethanol in 100 volumes of final solution) EtOH is given by $pH^* = R - 0.15$, in which R equals the reading of the pH-meter. Further details and an example of the calculation have been described in previous publications of our laboratory [9]. The difference between pK_a^* (1) and pK_a^* (2) for the dicarboxylic acids is too small to be determined using this method. For these acids averaged values from measurements at 1/3 and 2/3 neutralization have been given. Relative experimental errors in pK_a^*-values are less than 0.03 pK-unit, unless stated otherwise.

Results and discussion

Preparation of the π-(tricarbonylchromium)benzoic acids

Alkaline hydrolysis of the methyl π-(tricarbonylchromium)benzoates is easily achieved in most cases, since the rate of alkaline hydrolysis of the benzoates is increased considerably upon coordination with the $Cr(CO)_3$ group (methyl benzoate, $k \sim 0.008\ M^{-1}\ sec^{-1}$; methyl π-(tricarbonylchromium)benzoate, $k \sim 0.63\ M^{-1}\ sec^{-1}$) [13]. The strongly sterically hindered methyl esters of 2,4,6-trimethyl- and 2-t-butyl-π-(tricarbonylchromium)benzoic acid resisted both base and dilute acid catalysed hydrolysis. Application of the concentrated sulfuric acid technique, which is known to hydrolyse methyl mesitoate conveniently [14], caused decomplexation within a few seconds and subsequent hydrolysis. Ultimately, 2,4,6-trimethyl-π-(tricarbonylchromium)benzoic acid was obtained in 26% yield *, by the reaction of 1-bromo-2,4,6-trimethyl-π-(tricarbonylchromium)-benzene with n-butyllithium in pentane followed by carbonation. So far, various attempts to prepare 2-t-butyl-π-(tricarbonylchromium)benzoic acid have been unsuccessful.



Thermodynamic dissociation constants of the benzoic acid series (ligands)

The dissociation constants of some monoalkylsubstituted benzoic acids have been published previously [17]. These and other dissociation constants determined in our laboratory [18] are given in Table 2. The data show that the

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* The low yield is probably a consequence of the occurrence of competing reactions, such as alkylation and metallation of the complexed benzene nucleus [15,16].

TABLE 2

THERMODYNAMIC DISSOCIATION CONSTANTS[a] OF SUBSTITUTED BENZOIC ACIDS AND π-(TRICARBONYLCHROMIUM)BENZOIC ACIDS

No.	Substituent(s)	pK_a^*		ΔpK_a^*
		Ligand	Complex[b]	
1	None	5.48	4.52[c] *4.63*	0.96
2	2-Me	5.51	4.86	0.65
3	2-Et	5.49	4.93	0.56
4	2-i-Pr	5.38	4.80	0.58
5	2-OMe	5.52	4.83	0.69
6	3-Me	5.60	4.50 *5.74*	1.10
7	3-Et	5.65	4.57	1.08
8	3-i-Pr	5.71	4.59 *5.02*	1.12
9	3-t-Bu	5.72	4.68	1.04
10	3-OMe	5.37	4.24	1.13
11	3-Ph	5.46	4.44	1.02
12	3-F	5.04	4.25	0.79
13	3-Cl	5.01	4.09	0.92
14	3-Br	4.97	4.22	0.75
15	3-COOH	(4.72)[d]	(3.97)[d]	0.75
16	3-CF_3	4.89	4.06	0.83
17	4-Me	5.69	4.61 *5.57*	1.08
18	4-neoPent	5.72	4.60	1.12
19	4-Et	5.70	4.57 *5.42*	1.13
20	4-i-Pr	5.71	4.56 *5.36*	1.15
21	4-t-Bu	5.69	4.46 *5.32*	1.23
22	4-CEt_3	5.76	4.45	1.31
23	4-NMe_2	6.40	5.25	1.15
24	4-OMe	5.79	4.62	1.17
25	4-Ph	5.45	4.54	0.91
26	4-Cl	5.07	4.24	0.83
27	4-COOH	(4.49)[d]	(3.75)[d]	0.74
28	4-CF_3	4.70	3.90	0.80
29	3-(π-[$Cr(CO)_3$]Ph)	5.24	4.38	0.86
30	4-(π-[$Cr(CO)_3$]Ph)	5.13	4.37[e]	0.76
31	2,4,6-Me_3	5.00	4.19[e]	0.81
32	3,4-$(OMe)_2$	5.64	4.35	1.29
33	3,5-Me_2	5.74	4.47	1.27
34	3,5-t-Bu_2	5.94	4.80	1.14
35	3,5-$(OMe)_2$	5.26	4.08	1.18
36	3,4,5-$(OMe)_3$	5.26	3.86	1.40

[a] Measured in 50% aqueous ethanol (i.e. 50 volumes of absolute ethanol in 100 volumes of final solution) at 25.0°C. [b] The values given in italics are taken from ref. 5. [c] Values reported previously were 4.77 [4] and 4.52 (41% ethanol) [3]. [d] Averaged values from measurements at 1/3 and 2/3 neutralisation. [e] Duplicate measurements differ by 0.06 pK_a-unit.

influence of an alkyl substituent on the dissociation equilibrium is generally small. In the 2-alkylsubstituted benzoic acids (where variations are most pronounced), increasing bulkiness of the alkyl group results in increasing acidity. This is usually explained by a combination of opposing effects [19,17]: (i) steric inhibition of resonance resulting in an increased acidity and (ii) steric inhibition to solvation of the carboxylate anion, leading to a decrease in acidity. For the 3-alkylsubstituted benzoic acids steric inhibition to solvation of the carboxylate anion might cause the small decrease in acidity with increasing bulk of the alkyl group (cf. also ref. 17). The dissociation constants of the 4-alkylsubstituted benzoic acids differ only slightly.

The difference between the effects of the 3- and 4-methoxy group on the dissociation constant of benzoic acid is in accord with "through-resonance" theory [20]. The pK_a^*-values of both 3,4- and 3,5-dimethoxybenzoic acid are well predicted by additivity of the substituent parameters. On the other hand, additivity no longer holds on further substitution to 3,4,5-trimethoxybenzoic acid. This can be ascribed to a decrease in resonance interaction of the central methoxy group and the aromatic ring; steric requirements of the neighbouring methoxy groups prevent the central methoxy group from being coplanar with the benzene ring [21].

The pK$_a^*$-values for the substituted benzoic acids correlate excellently with the substituent parameters, σ_m, $\sigma_p{}^n$ and $\Delta\sigma_R{}^+$ [20], in terms of the Yukawa—Tsuno equation. Correlation data are given in Table 3.

From the pK_a^*-values of the benzoic acids, carrying a π-(tricarbonylchromium)-phenyl group as the substituent, the σ-values of this group were obtained using the parameters for the benzoic acids series given in Table 3. The results are given in Table 4, together with δpK_a^*-values and σ-values from IR data on the corresponding methyl esters. Clearly, the electron-withdrawing effect of the phenyl group is increased upon introduction of the $Cr(CO)_3$ group (cf. refs. 12 and 22); viz. by 0.22 and 0.32 pK_a^*-unit for the 3-Ph and 4-Ph group, respectively The present results, however, contradict earlier proposals [23,1] for a positive mesomeric effect of the π-[$Cr(CO)_3$]Ph group.

Thermodynamic dissociation constants of the π-(tricarbonylchromium)benzoic acid series

The thermodynamic dissociation constants of the substituted π-(tricarbonylchromium)benzoic acids together with the values reported recently by Ashraf and Jackson [5] are listed in Table 2. It is obvious from a comparison that the two series of pK_a^*-values differ substantially. Exploratory pK_a^*-measurements showed that exposure of a solution of the complex to diffuse daylight leads to decomposition [8]; the solution becomes opaque. Decomposition leads to enhanced pK_a^*-values, since it produces an equimolar quantity of the corresponding benzoic acid. Perhaps this decomposition has misled earlier investigators.

As shown previously [3,4,5], π-(tricarbonylchromium)benzoic acid is a

TABLE 3

DATA ON THE CORRELATION BETWEEN pK_a^*-VALUES OF THE BENZOIC ACID SERIES AND SUBSTITUENT PARAMETERS

$\log K/K^0 = \rho(\sigma + r\Delta\sigma_R{}^+)$

Series[a]	ρ	r	Increment	Correlation coeff.	S.d.
Benzoic acids	1.405 ± 0.057	0.245 ± 0.034	5.497 ± 0.015	0.991	0.056
π-(Tricarbonylchromium)-benzoic acids	0.895 ± 0.089	0.446 ± 0.105	4.437 ± 0.023	0.955	0.088

[a] $n = 21$; R = H, 3-Me, -Et, -i-Pr, -t-Bu, -OMe, -Ph, -F, -Cl, -Br, -CF_3, 4-Me, -Et, -i-Pr, -t-Bu, -NMe_2, -OMe, -Ph, -Cl, -CF_3 and 3,5-Me_2.

TABLE 4

pK_a^*-VALUES FOR SOME SUBSTITUTED BENZOIC ACIDS AND CORRESPONDING SUBSTITUENT PARAMETERS

Substituent (R)	δpK_a^{*} [a]	σ	σ [b]
3-Ph	0.02	0.03	0.10
3-(π-[Cr(CO)$_3$]Ph)	0.24	0.18	0.29
4-Ph	0.03	0.03	−0.07
4-(π-[Cr(CO)$_3$]Ph)	0.35	0.26	0.14

[a] $\delta pK_a^* = pK_a^*(H) - pK_a^*(R)$. [b] From ester carbonyl data [1].

stronger acid than benzoic acid and this has been rationalized as due to the electron-withdrawing effect of the $Cr(CO)_3$ group. The increment in pK_a^*-value upon complexation, denoted as ΔpK_a^*, amounts to ~1.2 for the electron-releasing and to ~0.8 for the electron-withdrawing *meta* and *para* substituents. The pK_a^*-values and the electronic substituent parameters, σ_m, $\sigma_p{}^n$ and $\Delta\sigma_R{}^+$ [20], correlate only poorly in terms of the Yukawa—Tsuno equation (see Table 3).

In accordance with results from previous reports [1,13,23—27], it is found that the π-(tricarbonylchromium)benzoic acid series is less sensitive to substituent effects than the benzoic acid series. This is also illustrated in Fig. 1, in

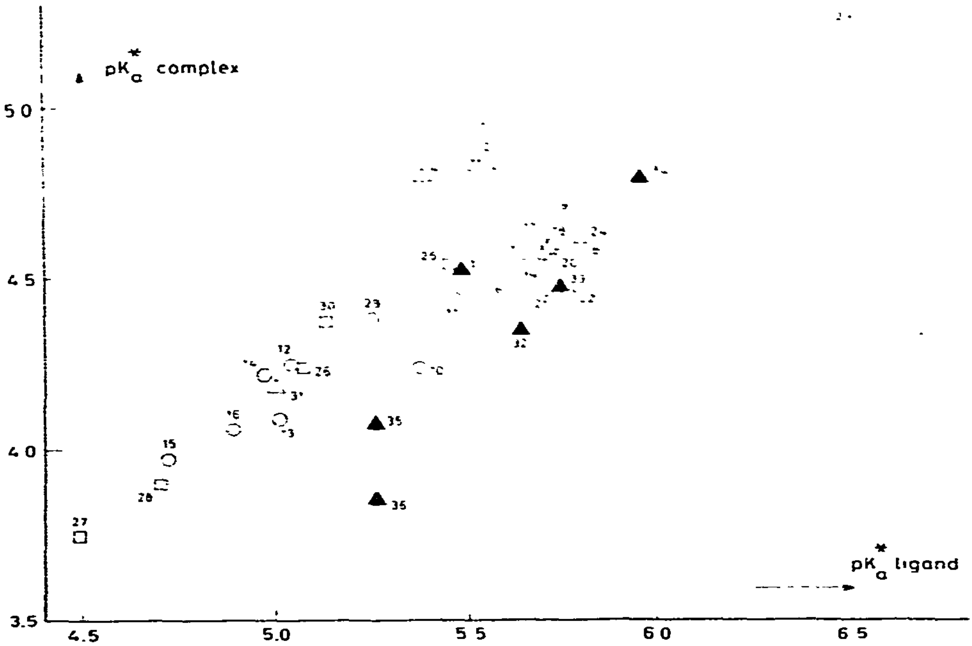
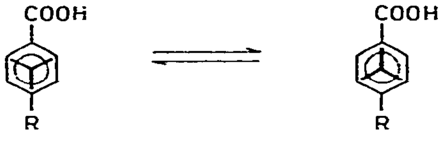


Fig. 1. Plot of pK_a^*(complex) vs. pK_a^*(ligand) for the π-(tricarbonylchromium)benzoic acids. The numbering refers to the numbering given in Table 2. △, ○ and □ denote *ortho*, *meta* and *para* substitution, respectively. The other compounds are given by ▲.

which the dissociation constants of the complexes have been plotted vs. the dissociation constants of the free ligands. Fig. 1 shows a considerable scatter, which we regard as largely being confined to the alkyl- and methoxy-substituted derivatives.

The pK_a^*-values of the *para* alkylsubstituted π-(tricarbonylchromium)benzoic acids show rather large variations in comparison with those of the corresponding benzoic acids. Examination of the ΔpK_a^*'s upon complexation suggests there is a relation between the size of the *para* alkyl substituent and ΔpK_a^*, i.e. increasing the size of R, from R = Me to R = CEt$_3$, the acidity is enhanced. For the *meta* alkylsubstituted benzoic acid complexes, however, an increase of the bulkiness of the *meta* substituent leads to a very small decrease in acidity. Similar sterical substituent effects were also observed in Part III [1] of this series and were tentatively ascribed [5,1,2] to influences of R on the preferred conformation of the $Cr(CO)_3$ group * with respect to the arene ring. The conformational proposals were based upon a conformational equilibrium between conformations I and II and were supported by ^{1}H NMR spectroscopic results [2].



I II

The same arguments can be applied to the corresponding benzoic acid complexes, since the substituent character of a COOH group resembles that of the COOMe group. Thus conformation I should be favoured for R = 4-Me and conformation II for R = 4-CEt$_3$ (cf. the results from X-ray work for R = 4-t-Bu [28] and for R = 3-Me (benzoate anion) [29]).

The relationship between the substituent effect upon complex formation reported here (ΔpK_a^*) and in Part III [1] ($\Delta\nu$(CO)) is visualized in Fig. 2. The correlation is satisfactorily for the *para* alkylsubstituted derivatives, whereas a somewhat less satisfactory correlation is obtained for the *meta* alkylsubstituted derivatives. However, it should be considered that solvation effects upon the dissociation constants should be taken more seriously than the solute—solvent effects upon the CO wavenumbers measured in isooctane [1]. The solvation effects upon the pK_a^* are expected to increase with decreasing distance between the substituent and the reaction centre, which may explain the disturbance of the correlation for the *meta* substituents (Fig. 2). The relatively low acidities of 2-alkyl-π-(tricarbonylchromium)benzoic acids ($\Delta pK_a^* \sim 0.6$) can be ascribed to a more pronounced steric inhibition of solvation of the corresponding benzoate anions. The accessible sphere around the COO^- group is reduced substantially by the effective bulkiness of the $Cr(CO)_3$ group and the alkyl group together.

In contrast with the results obtained for the free methoxy-substituted benzoic acids, the substituent effects on the pK_a^* in the corresponding $Cr(CO)_3$ complexes

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[*] Recent X-ray work [30] on some alkylsubstituted π-(tricarbonylchromium)benzenes provides additional support for these steric effects.

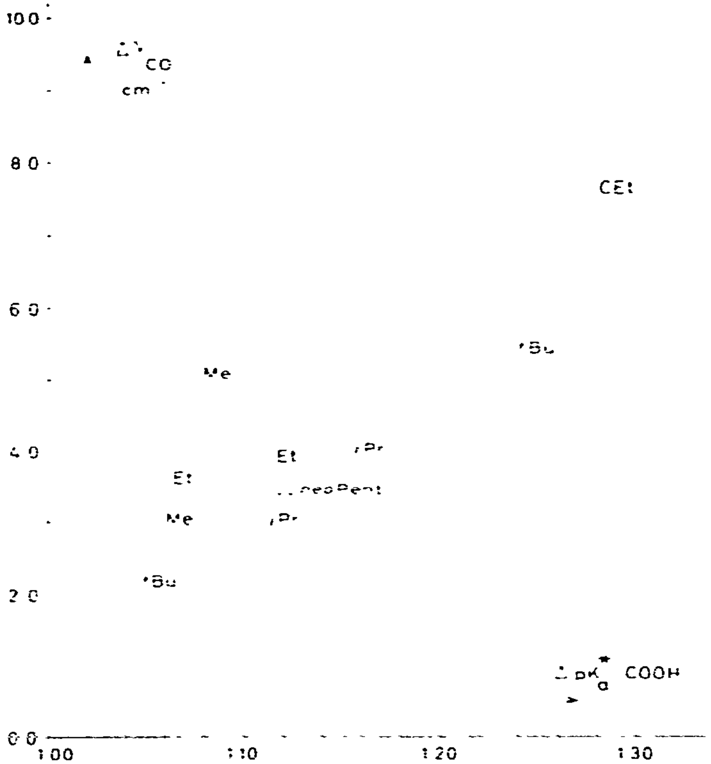

Fig. 2. Correlation of $\Delta\nu$(CO) of the methyl π-(tricarbonylchromium)benzoates [1], and ΔpK_a^* of the π-(tricarbonylchromium)benzoic acids.   and   represent *meta* and *para* substitution, respectively.

are far from additive. It is likely that both conformational effects of the $Cr(CO)_3$ group and solvation effects are involved in this. Of course, similar effects can also be operative in the other complexes investigated here.

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