Journal of Organometallic Chemistry, 348 (1988) 219–233
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Arene transition metal complexes in reactions with nucleophilic reagents

XIX *. Transannular substituent effects in arene-chromium and iron complexes

V.V. Litvak *, **P.P. Kun, V.D. Shteingarts**

Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 630090, Lavrentiev Ave, 9 (U.S.S.R.)

(Received December 15th, 1987)

Abstract

As a result of coordination of chlorobenzene derivatives with the $(\eta\text{-}C_6H_6)Cr^+$ fragment, the rate of methoxydechlorination was found to increase 14 fold. The effects of the transannular substituent on the rate of methoxydechlorination of $(\eta\text{-}C_6H_5Cl)(\eta\text{-}C_6H_5X)Cr^+A^-$ complexes (**1**) and on the dissociation constants of $(\eta\text{-}C_6H_5CO_2H)(\eta\text{-}C_6H_5X)Cr^n$ acids $n = 0$ (**2**), 1 + (**3**) has been studied. A strong effect of X in the above reaction series has been found, which is defined by the linear correlation equations using the σ_p, σ^0 and σ_R constants for complexes **1**, **2** and **3** respectively. The arene-chromium and -iron complexes show a general tendency to increase the mesomeric contribution to the transannular substituent effect with an increase in the electron deficiency in the framework transmitting this effect. Comparison of the effects of X in complexes **1**, **2** and **3** leads to the conclusion that there is an intermediate-like transition state in the methoxydechlorination of complexes **1**, apparently proceeding with intermediate formation of metallorganic analogues of Meisenheimer complexes.

Introduction

Activation of aromatic compounds towards reaction with nucleophiles by π-coordination with metal complex fragments opens up new possibilities in the chemistry of aromatic compounds. This necessitates more profound investigation of the kinetics of the reactions of π-arene transition metal complexes with nucleophiles [1].

---

* For part XVIII see ref. [40].

0022-328X/88/$03.50

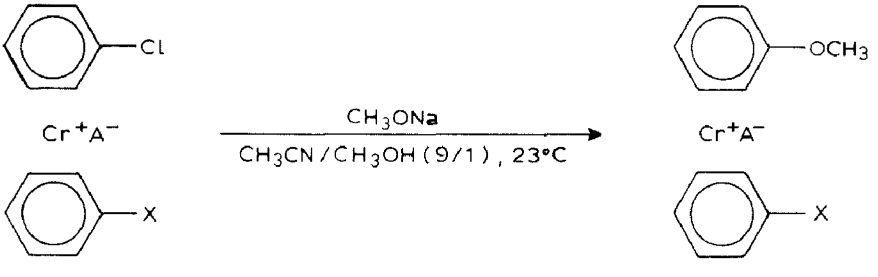
One of the key problems involved is determining the contribution to the strong activating effect of the metal complex fragments with the aim of finding quantitative correlations between their nature and the reactivity of the π-arene complexes. One such contribution is the nature of other ligands which affect the reacting arene ligand through the metal atom. Earlier studies [2–4] have reported a general method of synthesis of bis-arene-chromium complexes with different substituents in the unreacting ligand, which allows a quantitative description of transannular substituent effects on the reactivity of complexes of this type. The purpose of this work is to develop a quantitative relationship for the transannular substituent effects on the rate constants of the reactions of complexes **1** with sodium methoxide in comparison with those on the strength of bis-arene-chromium (0, 1 +) carboxylic acids of types **2** and **3** in terms of the correlation analysis.

Results and discussion

Regarding complex **1f** as an example, it has been found that coordination of chlorobenzene with the (η-C_6H_6)Cr(1 +) fragment raises the rate of chlorine substitution by the action of sodium methoxide 14-fold. This effect is comparable with the influence of two *ortho-para*-nitro groups in a non-coordinated arene.

With regard to this result, all the π-coordinated metal complex fragments studied up till now may be arranged according to their activating effect in the above reaction in the series: $Cr(CO)_3 < Mo(CO)_3 \leqslant Cr^+(C_6H_6) < Fe^+(C_5H_5) < Mn^+(CO)_3$ [1]. In this sequence the influence of the chromium cationic fragment is 4 times greater than that of the neutral $Cr(CO)_3$ group, and is only slightly smaller than that of other cationic fragments. Due to this, complex **1f** reacts with sodium methoxide under mild conditions and the respective methoxy derivative **4f** is formed in a high yield (93% after purification), the amount of chloride ion produced in the reaction nearing 100% in all cases.

The kinetic studies of methoxydechlorination of complexes of type **1** have revealed that differences in counter-ions (PF_6^- or BPh_4^-) have practically no effect on the reaction rate constant (Table 1, Nos. 1 and 2). As shown in ref. 5, the arenecyclopentadienyliron(1 +) and arenetricarbonylmanganese(1 +) complexes



(1a-1i) **(4a-4i)**

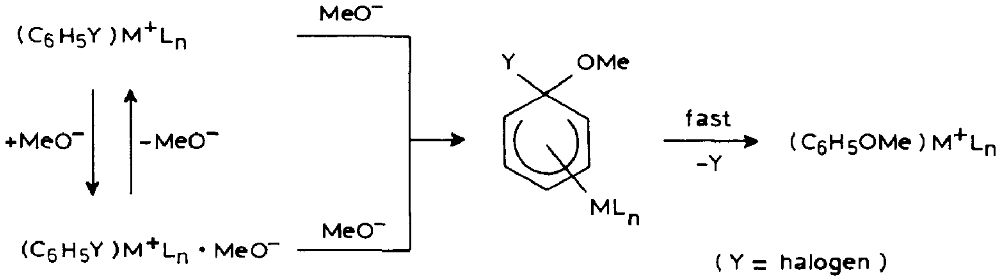
(X = NMe_2 (**a**) ; OPr-i (**b**) , OBu-n (**c**) , OMe (**d**) , CO_2Na (**e**) , H (**f**) , Cl (**g**) , CO_2Me (**h**) , CF_3 (**i**) ; $A^- = PF_6^-$, BPh_4^-)

Table 1

Influence of counter-ions and reagent concentrations on the rate constant of the reaction of bis(η-chlorobenzene)chromium(1 +) with sodium methoxide.

No.	Counter-ions of complexes	Reagent concentration (c, mol/l)		$\frac{c_{MeONa}}{c_{compl.}}$	Solvent	$k_{23^\circ C}$ (l/mol s)
		complexes ($c \times 10^3$)	MeONa			
1	PF_6^-	2.13	4.29×10^{-3}	2.0	MeCN/MeOH 9/1	9.9×10^{-1}
2	BPh_4^-	2.04	4.30×10^{-3}	2.1		9.8×10^{-1}
3	PF_6^-	1.07	1.46×10^{-3}	1.4		9.5×10^{-1}
4	PF_6^-	1.05	1.43×10^{-2}	14		9.9×10^{-1}
5	PF_6^-	6.01	2.60×10^{-2}	4.3	MeOH	1.1×10^{-2}
6	PF_6^-	6.21	1.06×10^{-1}	17		6.9×10^{-3}
7	PF_6^-	6.21	2.67×10^{-1}	43		5.3×10^{-3}

can form ionic pairs with the methoxyanion in methanol, less active (~ 0.5 times) in the substitution of halogen in the arene ligand than the free cations.



In the authors [5] opinion, this ion-pairing is the reason for the decreasing experimental value of the second order rate constant of methoxydechlorination of these complexes with the raising of the sodium methoxide concentration and the approach of this value to a constant. This might complicate the interpretation of the substituent effects on the rate of nucleophilic substitution of chlorine, which made us clarify in the case of complex **1g** whether the rate constant value of the above reaction depends on the concentration of sodium methoxide. As seen from Table 1 (cf. nos. 3 and 4, 5 to 7), when the reaction is carried out in acetonitrile/methanol, the 10-fold increase in sodium methoxide concentration does not change the rate constant value, whereas in methanol the value decreases with an increase in sodium methoxide concentration, as reported for the similar case in ref. 5. These results may be explained by practically complete dissociation in the acetonitrile/methanol mixture. According to ref. 6, solvation of the bis-arene-chromium cationic complex by an aprotic dipolar solvent is rather efficient.

The rate constant values for the reaction of complexes **1** with sodium methoxide given in Table 2 indicate that variation of the substituent in one arene ligand strongly influences the mobility of chlorine as a leaving group in another. Qualitatively this influence is represented by the series: $NMe_2 < OPr\text{-}i < OBu\text{-}n < OMe < CO_2^- < H < CO_2Me < CF_3$, the difference in the reaction rate constant values for the extreme members of the series being more than 4 fold [7]. This sequence (excluding the CO_2^- group) is also typical for the *para*-substituent effect directly

Table 2

Rate constants for the reaction of complexes (η-C_6H_5Cl)(η-C_6H_5X)Cr^+ BPh_4^- with sodium methoxide [a] and the pK_a values of bis-arene-chromium(0, 1 +)carboxylic acids [b]

No.	Substituents	k (l/mol s)	pK_a Values		
			Acids of type 3	Acids of type 2	p-$XC_6H_4CO_2H$ [24]
1	NMe_2	1.6×10^{-4}	–	–	–
2	OPr-i	9.3×10^{-4}	4.15	–	–
3	OBu-n	2.4×10^{-3}	4.05	–	–
4	OMe	3.2×10^{-3}	4.61	6.00	5.79
5	Me	–	3.76	–	5.69
6	Co_2^{-c}	3.0×10^{-2}	3.52	5.80	–
7	H	1.3×10^{-1}	3.65	5.96	5.48(5.68 [23])
8	Cl	9.9×10^{-1}	3.80	5.72	5.07
9	CO_2Me	1.7	3.53	5.55	–
10	CO_2H [c]	–	3.49	5.56	4.79
11	CF_3	3.6	3.46	5.41	4.70

[a] Solvent: MeCN/MeOH (9/1 by volume), 23°C. [b] 50% ethanol, 25°C. [c] The pK_a values take into account the statistical coefficient.

through the benzene ring in the nucleophilic substitution of halogen in non-coordinated arenes [8,9]. The electron-donating effect of the CO_2^- group in the reaction of complexes **1**, unlike its electron accepting effect in a similar reaction of non-coordinated nitrohalobenzenes [9], may arise from the presumably specific direct interaction between the CO_2^- group and chromium in the transition state of the limiting stage of the reaction and from the use of different solvents in the reactions of coordinated and non-coordinated arenes. On passing from methanol (for nitrohalobenzenes) to the acetonitrile/methanol (9/1) system, the association resulting from hydrogen bonding of CO_2^- with methanol decreases, which leads to the increased charge on the carboxylate group and its enhanced electron-donating ability.

To determine the character of the substituent effects and estimate the reaction rate sensitivity to these effects, we have studied the possibility of correlating the logarithm of rate constants with constants representing various types of substituent effects in non-coordinated arenes (Table 3).

Comparison of the r and s values listed in Table 4 indicates that the use of σ constants corresponding to one type of effect (inductive or resonance) does not lead to linear correlations. It is however essential that on passing from the Taft σ_i constants to the Hammet σ_m constants taking into account, along with the inductive and field effects, the mesomeric effect as well (0.33 M) [10,15], the correlation coefficient r increases sharply. In the case of σ_R constants r proceeds to grow but still is not high enough to give a satisfactory linear correlation. Satisfactory linear correlations (for σ_p^- or σ_p^0) and the best (σ_p) (Fig. 1) are observed only for the σ constants representing combinations of mesomeric and inductive effects with the former predominating. The fact that the best correlation is that with σ_p but not σ_p^-, apparently indicates the smaller contribution of the direct polar conjugation than in the similar reactions of non-coordinated arenes [8,16].

Thus the results of correlation analysis of log k values indicate that the transannular substituent effect is realised by both the inductive and mesomeric mechanisms

Table 3

Values of substituent constants used in the correlation analysis

Substituent	σ_i[11]	σ_m[12]	σ_p^0[12]	σ_p[12]	σ_p^+ [12]	σ_p^- [11]	σ_R [a]	F[13]	R[13]
NMe_2	0.1	−0.05	−0.44	−0.6 [b]	−1.7	−0.83	−0.7	—	—
OPr-*i*	0.28 [b]	0.1 [b]	−0.16 [d]	−0.45	−0.986[13]	−0.45	−0.73	0.483	−0.724
OBu-*n*	0.31 [b]	0.1 [b]	−0.13 [d]	−0.32	−0.783[13]	−0.32	−0.63	0.411	−0.551
OMe	0.29	0.115	−0.12	−0.268	−0.648	−0.27	−0.558	0.413	−0.500
Me	−0.08	−0.069	−0.15	−0.17	−0.256	−0.17	−0.09	−0.052	−0.141
CO_2^-	−0.05	−0.1	-	0.0	0.109	0.32 [b]	0.05	−0.221	0.124
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl	0.47	0.37	0.27	0.227	0.035	0.227	−0.243	0.690	−0.161
CO_2Me	0.30	0.32	0.46	0.39	0.49	0.636	0.09	0.552	0.140
CO_2H	0.32 [c]	0.37	0.41 [b]	0.45	0.472	0.728	0.13	0.552	0.140
CF_3	0.41	0.43	0.53 [d]	0.54	0.582	0.65 [b]	0.13	0.631	0.186

[a] Calculated from the equation $\sigma_R = \sigma_p - \sigma_i$. [b] The values are taken from ref. 10. [c] The values are taken from ref. 14. [d] Calculated from the equation $\sigma_p^0 = \sigma_R^0 + \sigma_i$. The σ_R^0 values are taken from ref. 14.

Table 4

Parameters of correlations between rate constant. Logarithms for the reaction of complexes of type **1** with sodium methoxide and substituent σ constants

σ-constants	ρ	r	s
σ_i	3.97	0.410	1.53
σ_m	7.69	0.826	0.94
σ_p^0	4.83	0.964	0.48
σ_p	3.99	0.991	0.23
σ_p^+	2.04	0.964	0.45
σ_p^-	2.92	0.945	0.55
σ_R	3.35	0.876	0.81

and is characterised by about the same sensitivity constant (3.99) as in the case of similar reactions of 4-X-2,6-dinitrochlorobenzenes (3.7 at 25 °C [9]), which are close in their reactivity to complexes of type **1**. Besides, these results do not contradict the earlier conceptions [2,3,17–21] about the mechanism of the reactions of π-coordinated arenes with nucleophilic reagents and allow us to adopt for the above reaction a scheme involving the intermediate formation of complex 5.

In the case of an intermediate-like transition state, the character of substituent effects on the nucleophilic substitution rate is expected to be different from that observed for the starting arene chromium complexes and is similar to that for the systems like the neutral intermediate **5**. As a reaction series modelling substituent effects in substrates, it is possible to consider dissociation of bisarenechromium (1 +) carboxylic acids. Since the complexes **5** are neutral compounds it might be possible that in the case of the late (intermediate-like) transition state of methoxydechlorination the substituent effects are modelled by those on the dissociation of bisarenechromium(0) carboxylic acids.

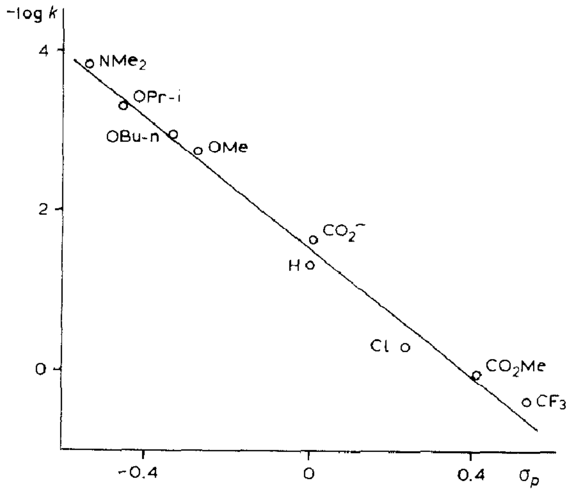


Fig. 1. Correlation between log k values and substituent σ_p constants for the reaction of complexes of type **1**.

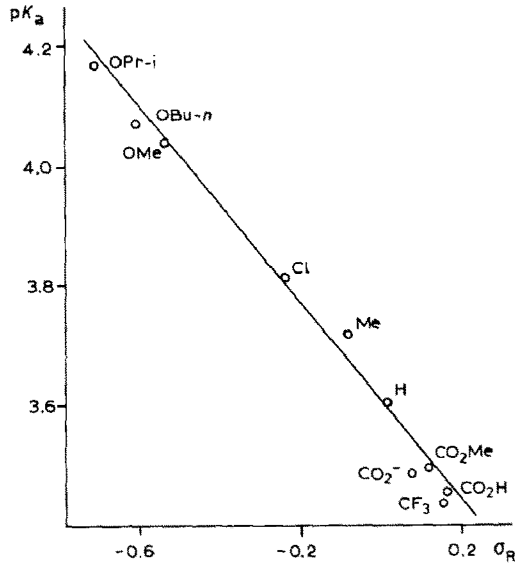
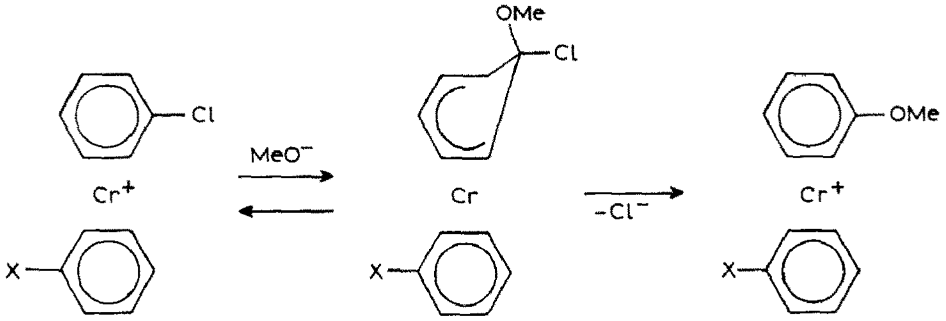
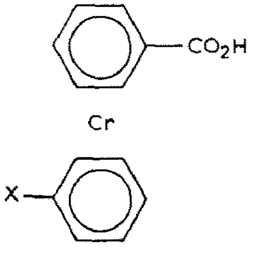


Fig. 2. Correlation between pK_a values of acids (η-$C_6H_5CO_2H$)(η-C_6H_5X)$Cr^+ PF_6^-$ substituent σ_R-constants.

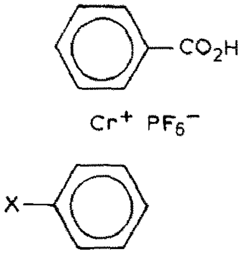


(1) (5) (4)

In this connection we have studied the transannular substituent effects on pK_a values of acids of types **2** and **3** whose synthesis is reported [4,7,22].



(2)



(3)

(Complexes **2**: X = OMe, H, CO_2^-, Cl, CO_2Me, CO_2H, CF_3. Complexes **3**: X = OPr-i, OBu-n, OMe, Me, H, CO_2^-, Cl, CO_2Me, CO_2H, CF_3.)

Table 5

Comparison of the pK_a values of coordinated and non-coordinated benzoic acids (50% ethanol, 25 ° C)

No	Acid	pK_a
1	$(\eta\text{-}C_6H_5CO_2H)(\eta\text{-}C_6H_6)Cr$	5.96
2	$C_6H_5CO_2H$	5.68 [23]
3	$(\eta\text{-}C_6H_5CO_2H)Cr(CO)_3$	4.77 [23], 4.52 [24]
4	$p\text{-}NO_2C_6H_4CO_2H$	4.48 [23]
5	$(\eta\text{-}C_6H_5CO_2H)(\eta\text{-}C_6H_6)Cr^+ PF_6^-$	3.65
6	$(\eta\text{-}C_6H_5CO_2H)(\eta\text{-}C_5H_5)Fe^+ PF_6^-$	3.05 [25]

The chosen substituents X allow the estimation of both the inductive and mesomeric contributions, as well as the effect of direct polar conjugation with the reaction centre. It is important that some substituents (CO_2^-, Cl, OMe) have opposing inductive and mesomeric effects, and if one of them is suppressed, quite a pronounced manifestation of the character of the transannular substituent effects on the dissociation constants of acids will be expected.

Table 2 lists the pK_a values determined by potentiometric titration of 50% ethanol solutions of acids at 25 ° C in argon. Determination of these values for compounds of type **3** might be complicated by their hydrolysis as salts. But it has been found that the solutions of complexes containing no carboxylic groups, such as bis(η-chlorobenzene)chromium(1 +) hexafluorophosphate, are neutral, which indicates that there are no such complications.

The pK_a values for benzoic acid coordinated with the $(\eta\text{-}C_6H_6)$Cr(0, 1 +) fragments considerably expand the general picture of the influence of π-coordination and charge of metal complex fragments on the strength of aromatic acids. As seen from Table 5 coordination of benzoic acid with the neutral fragment $(\eta\text{-}C_6H_6)$Cr even decreases the dissociation constant, which indicates the weak electron-donating effect of this fragment (cf. nos. 1 and 2), comparable with the effect of methyl in non-coordinated acids. This result is in agreement with the data of IR studies of neutral bis-arene-chromium complexes [26,27]. At the same time coordination with the cationic fragment $(\eta\text{-}C_6H_6)Cr^+$ increases the dissociation constant of benzoic acid about two times (cf. nos. 2 and 5). The effect of this fragment is 4 times as weak as that of the group $(\eta\text{-}C_5H_5)Fe^+$, but an order stronger than that of the tricarbonylchromium group. The latter is comparable with the influence of the *para*-nitro group (cf. nos. 3, 4, 6). These data suggest that the positive charge makes the greatest contribution to the effect of the $(\eta\text{-}C_6H_6)Cr^+$ fragment in the reaction of nucleophilic substitution of halogen in the arene ligand of bisarene chromium (1 +) complexes.

Investigation of the transannular substituent effects on the dissociation constants of acids of type **3** revealed some qualitative differences from the substituent effects on the strength of non-coordinated benzoic acids. Though in this series, as in the series of non-coordinated compounds, the strength of acid increases with the electron-accepting ability of the substituent, the general tendency is not true for the carboxylate group and the chlorine atom (nos. 6 and 8, Table 2). Indeed, in contrast to the non-coordinated acids, in this series the chlorine atom shows an electron-donating effect comparable with that of the methyl group (cf. nos. 5 and 8) and the carboxylate group has an electron-accepting effect comparable with that of the

Table 6

Correlation analysis of the transannular substituent effects on the pK_a values of acids of types **2**, **3** and ferrocenecarboxylic acids (η-$C_5H_4CO_2H$)(η-C_5H_4X)Fe

Type of constant	Acids of type 3			Acids of type 2			Ferrocenecarboxylic acids (η-$C_5H_4CO_2H$)(η-C_5H_4X)Fe		
	ρ	r	s	ρ	r	s	ρ	r	s
σ_i	−0.096	0.067	0.269	0.604	0.541	0.203	1.167	0.823	0.185
σ_m	0.392	0.300	0.257	0.821	0.775	0.153	1.263	0.944	0.106
σ_p^0	0.549	0.812	0.127	0.894	0.989	0.040	0.980	0.964	0.087
σ_p	0.636	0.869	0.133	0.727	0.962	0.066	0.926	0.949	0.102
σ_p^+	0.446	0.965	0.071	0.468	0.890	0.106	0.552	0.822	0.174
σ_p^-	0.529	0.912	0.111	0.555	0.937	0.085	0.658	0.936	0.115
σ_R	0.749	0.986	0.044	0.589	0.682	0.177	–	–	–
σ_R^+	0.438	0.986	0.044	0.437	0.468	0.214	–	–	–
$aF + bR$[a]	0.01F+0.76R	0.995	0.030	0.41F+0.70R	0.963	0.073	0.58F+0.61R	0.948	0.099

[a] The correlation was made according to the formula p$K_a = aF + bR + c$.

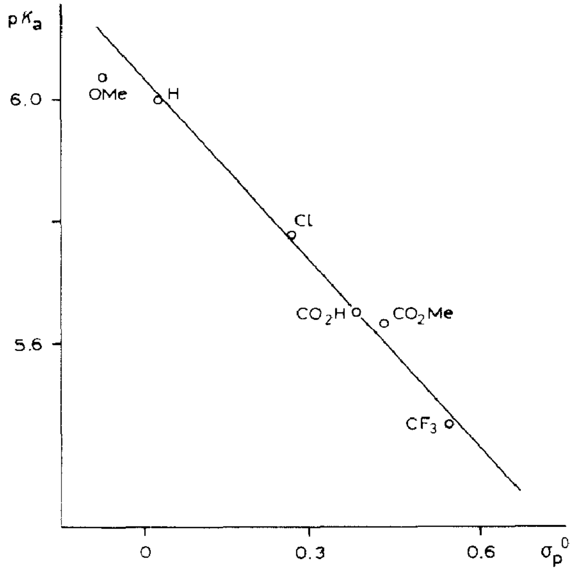


Fig. 3. Correlation between pK_a values of acids (η-$C_6H_5CO_2H$) (η-C_6H_5X)Cr and substituent $\sigma_p{}^0$-constants.

methylcarboxylate group (cf. nos. 6 and 9). By contrast with the results for the cationic acids of type **3**, the substituent effects on the pK_a of uncharged acids of type **2** and non-coordinated substituted benzoic acids are qualitatively similar (Table 2).

In order to determine the character of the substituent effects on the strength of acids of types **2** and **3**, we analysed the possibilities of linear correlations between the pK_a values of these acids and various sets of substituent constants (Table 3). Comparison of the r and s values (Table 6) shows that linear correlations for acids of type **3** are observed only in the case of σ constants corresponding mainly to the resonance effect of substituents (σ_R, $\sigma_R{}^+$ (Fig. 2) and $\sigma_p{}^+$). This is also confirmed by the existence of a correlation with the combined parameter 0.76R + 0.01F. The use of constants representing only (or for the most part) the inductive effect (σ_i, σ_m) or the comparable contributions of the inductive and resonance effects of substituents (σ_p, $\sigma_p{}^0$) does not lead to a satisfactory linear correlation.

For the uncharged acids of type **2** the case is different (Table 6). The use of σ-constants specifying the effect of one type (σ_i, σ_m, σ_R) does not lead to linear correlations between the pK_a values and these σ-constants. A satisfactory correlation is observed only in the case of σ-constants representing a combination of the inductive and mesomeric effects of substituents ($\sigma_p{}^0$, σ_p). The fact that the best correlations are those with the $\sigma_p{}^0$ values (Fig. 3) apparently indicates the absence of a contribution of the direct polar conjugation between the substituent and the reaction centre in the dissociation of acids of type **2**. This is in agreement with a significant decrease in the R contribution in the corresponding two-parameter correlation as compared with acids of type 3.

Thus the mechanism of transmission of substituent effects in the dissociation of acids of type **2** is similar to that in the reactions of non-coordinated arenes having no conjugation of the substituent with the reaction centre, for example in the dissociation reactions of phenylacetic or arylphosphonic acids [10]. Detachment of the carboxy group from the aromatic ligand containing the substituent by the $Cr(\eta\text{-}C_6H_5)$ fragment has an effect similar to the introduction of the CH_2 group between the *para*-substituted phenyl radical and the reaction centre. At the same time, a better correlation of pK_a with $\sigma_p{}^0$ constant of substituents than with σ_i or σ_m presumably suggests that the arene ligand containing the substituent transmits its effect mainly by the conjugation mechanism. In contrast with the uncharged complexes **2**, the character of substituent effects on the strength of cationic acids of type **3** is similar to that in the reactions leading to electron-deficient systems like benzyl cations or arenonium ions [28].

On comparison of our results with literature data on the character of substituent effects in bisarene chromium complexes, our attention was drawn by the statement that the ^1H and ^{13}C NMR chemical shifts of the non-fluorinated benzene ring of $(\eta\text{-}C_6H_6)Cr(\eta\text{-}C_6F_xH_{6-x})$ complexes ($x = 0$, 4–6) correlate with σ_m constants of fluorine [29]. However, as the effect of fluorine atoms is additive, the characteristics of the benzene ligand should correlate with any values taken as the parameters specifying fluorine influence. At the same time, the combined analysis of the transannular effects of fluorine atoms and carbomethoxyl groups on the chemical shift values of the benzene ligand, reported in the same study [29], reveals that the best correlation is observed in the case of $\sigma_p{}^0$ constants ($r = 0.980$ for $\delta(^1H)$ and 0.995 for $\delta(^{13}C)$; in the case of σ_m constants $r = 0.897$ for $\delta(^1H)$ and 0.986 for $\delta(^{13}C)$). Thus the character of transannular substituent effects in this case is similar to that found by us for the pK_a values of uncharged bis-arene-chromium carboxylic acids of type **2**. It was shown for arenechromium tricarbonyl complexes [30–32] that the influence of arene ligand substituents on the force constant of the carbonyl ligand C–O bond is well defined by correlation with the σ_p and $\sigma_p{}^0$ constants of the substituents. As follows from these data, the character of transannular substituent effects in bis-arene-chromium(0) complexes is similar to that in arene-chromium tricarbonyl complexes. Indeed, we found that between the pK_a values of acids of type **2** and changes in the force constant of the carbonyl ligand bond ($\Delta k^X_{CO} = k^X_{CO} - k^H_{CO}$) in arene-chromium tricarbonyl complexes under the influence of the arene ligand substituent X, averaged as shown in [30,31,33], there is a satisfactory linear correlation ($r = 0.977$, $s = 0.063$).

Thus the analysis of our results and the above literature data leads to the conclusion that with growth of the electron deficiency in the framework transmitting the transannular substituent effect in chromium arene complexes ($Cr^0 \rightarrow Cr^{\delta+} \rightarrow Cr^+$), the relative inductive contribution to the general substituent effect decreases and the relative resonance contribution increases.

Supposing that the consistencies revealed here may be of a general character, we considered the data concerning the substituent effects on some properties of iron π-complexes. The transannular substituent effects in arenecyclopentadienyliron complexes and ferrocene on the proton chemical shifts of the cyclopentadienyl ligand were shown to be well defined by the combination of the σ_i and $\sigma_R{}^0$ constants of substituents. It is not out of the question that in this case there is also an increase in the resonance contribution from ferrocene (the best correlation is with $0.39\sigma_i + 0.21\sigma_R{}^0$ [35]) to the charged arenecyclopentadienyliron complexes (the best correlation is with $0.46\sigma_i + 0.31\sigma_R{}^0$ [34]). Studying the transannular substituent effects on the pK_a values of ferrocenecarboxylic acids it was concluded [36] that for most substituents used they are of the inductive character. A limited number of pK_a values of ferrocenecarboxylic acids used in correlations with substituent σ_i and $\sigma_m{}^0$ constants (number of points $n = 6$), small correlation coefficients ($r = 0.936$ and 0.952 with the use of σ_i and $\sigma_m{}^0$ constants) and the literature data [37] indicating possible transmission of the resonance substituent effect on the strength of acids through the ferrocene framework prompted us to carry out a more detailed correlation analysis of pK_a values of ferrocenecarboxylic acids using various sets of substituent σ constants. In this analysis only the data of ref. 36 were used as they give dissociation constants for a much larger number of compounds than ref 37. Besides, the pK_a values of acids containing electron-accepting substituents significantly differ in refs. 36 and 37. As seen from Table 6, the best parameters are observed for the correlation with subsituent $\sigma_p{}^0$ constants ($n = 12$). Thus, in this reaction series there is also a certain resonance contribution to the transannular substituent effects which is similar in nature to the ones observed in the dissociation of acids of type **2**.

On the whole the results obtained in this treatment possibly indicate that in neutral arene chromium and iron complexes the metal complex fragment hinders transmission of the substituent conjugation effect to the reaction centre, like interposing the CH_2 group between the benzene ring and the functional group. But interaction of a substituent with the ligand in which it is located seems to occur to some extent by the conjugation mechanism (see also refs. 30, 31, 34). At the same time, an increase in the electron deficiency of the framework, the resonance contribution to the transannular substituent effect grows, which is especially evident in the dissociation reaction of bisarenechromium(1 +) carboxylic acids.

The above picture of substituent effects on the strength of acids **2** and **3** provides the basis for considering the question of the character of the transition state in the nucleophilic substitution in complexes of type **1**. The reactions with an early transition state may be expected to show chiefly the resonance substituent effects like those in the dissociation acids **3**. As a matter of fact substituent effects on the chlorine substitution rate in complexes **1** are best defined in terms of the correlation approach using the Hammet σ_p constants and between the log k values for this reaction and the pK_a values of bisarenechromium(1 +) carboxylic acids there is no linear dependence ($r = 0.845$, $s = 0.156$). These data suggest that the transition state in the nucleophilic substitution reaction is not early (reagent-like).

As shown above, the transannular substituent effects on the pK_a values of bisarenechromium(0) carboxylic acids, which, owing to the absence of charge, might model the intermediates and, respectively, late (intermediate-like) transition states for the nucleophilic substitution reaction of complexes **1**, are best defined in terms of the correlation approach with the help of $\sigma_p{}^0$ constants. This indicates a somewhat different character of substituent effects as compared to the halogen nucleophilic substitution in bisarenechromium(1 +) complexes, which shows a correlation of log k values with substituent σ_p constants. Actually, between the pK_a values of bisarenechromium(0) carboxylic acids and log k for the halogen substitution in complexes **1** there is no linear dependence ($r = 0.864$, $s = 0.66$). The analysis of possible reasons for this inconsistency reveals a number of essential differences between the reaction series being compared. Firstly, σ-complexes of type **5** are free radicals and the adopted diamagnetic model acids of type **2** are not isoelectronic with them. Secondly, σ-complexes of type **5** and bisarenechromium(0) carboxylic acids **2** differ in the character of one of the ligands; for the former this is the cyclohexadienyl ligand, for the latter, the arene one. Nucleophilic substitution with a late transition state might be more adequately modelled by the reactions producing stable σ-complexes **5** as a result of the nucleophilic addition to bis-arene-chromium(1 +) complexes or the dissociation of phenols and anilimum salts coordinated with the $(ArCr)^+$ fragment.

To sum up, the transformations of complexes **1** in nucleophilic substitution reactions are not adequately modelled by the dissociation reactions of bis-arene-chromium(0.1 +) carboxylic acids. At the same time, the general tendency shown above of the decreased resonance contribution of the transannular substituent effect with a decrease in the electron deficiency in the framework transmitting this effect, and differences in the character of substituent effects between all the reaction series studied here seem to indicate that in the transition state of nucleophilic substitution in complexes **1**, the substituent and the reaction centre are separated by a framework that is more similar in character to that in the electro-neutral intermediate of type **5** than in the starting system. This supposition is supported by the good correlation between the rate constant logarithms of chlorine nucleophilic substitution in complexes **1** and by changes in the force constant of the C–O bond of carbonyl ligands of arenechromium tricarbonyl complexes upon variation of the substituent in the arene ligand [31,32,34] ($r = 0.983$, $s = 0.35$).

Earlier, in the studies of substituent effects on the rate constant of chlorine nucleophilic substitution in the arene ligand of arenoceneiron(1 +) complexes reacting with substituted phenoxides [21], the intermediate-like transition state has also been suggested to be close to the intermediate σ-complex the π-coordinated analogue of Meisenheimer complexes. It seems that such a transition state is typical for the reactions of π-coordinated arenes with nucleophiles.

Experimental

The recording conditions for the IR, UV and ESR spectra of the complexes are described [4]. To determine the chloride ion content in the reaction solution, it was sampled and sodium methoxide was neutralised with sulphuric acid. The amount of chloride ion was determined by potentiometric titration with silver nitrate. The products of the reactions of complexes **1a**, **1d**, **1g** with sodium methoxide, complexes **4a**, **4d**, **4g** have been reported in our previous work [4], the characteristics of new compounds, **4b**, **4c**, **4e**, **4h**, are given in Table 7. The kinetic measurements procedure is described [3].

The pH measurements of acid solutions were carried out using the universal EV-74 ionometer with a glass electrode. As a reference electrode, the saturated calomel electrode was used. The pH scale was established according to standard buffer solutions of acidic potassium phthalate (pH 1.68) and potassium tetraoxalate (pH 4.01). The titrated solution was placed under argon, the solution temperature was kept at 25 ± 0.5 °C. 5–6 mg of the acid was dissolved in 30 ml of 50% (by volume) ethanol and titrated with an alcohol solution of sodium hydroxide. The pK_a values for monobasic acids were calculated according to the Cummler formula for three neutralisation degrees, 30, 50 and 70% [38]. For dihydridic acids the pK_{a1} and pK_{a2} values were calculated by the graphic method [39]. For each acid, 3 to 6

Table 7

Elemental analysis and spectral data for complexes of type $(\eta\text{-}C_6H_5X)(\eta\text{-}C_6H_5OCH_3)Cr^+ BPh_4^-$.

No. of Complex	X	Analysis (Found (calc.)(%))		ESR[a] $^aH(e)$	Spectral data λ_{max}(log e)	IR[b] ($\bar{\nu}$, cm^{-1})		
		C	H			Cr–Ar	C–C(Ar)	C–O
4b	OPr-*i*	77.84 (78.04)	6.48 (6.55)	3.7	347(3.78)	420,460	1445,1515	1245
4c	OBu-*n*	78.00 (78.21)	6.83 (6.72)	3.8	348(3.71)	430,470	1455, 1530	1250
4e	CO_2H	75.85 (75.88)	5.69 (5.70)	3.4	350(3.63)	425,475	1430, 1535	1265,1280, 1305
4h	CO_2Me	76.28 (76.10)	5.88 (5.90)	3.4	353(3.67)	425,475	1435, 1530	1260,1275, 1290

[a] The number of spectral lines for all the complexes is 9. [b] Positions of absorption bands corresponding to counter-ion vibrations are not given. The values of $\bar{\nu}$ (C=O) (cm^{-1}): 1715 (complex **4e**) and 1735 (complex **4h**).

titrations were carried out. The standard deviation for the pK_a values of acids **3** does not exceed ±0.03, of acids **2**, ±0.05.

References

1 V.V. Litvak, V.D. Shteingarts, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., (1983) 59.

2 V.V. Litvak, P.P. Kun, V.D. Shteingarts, Zh. Org. Khim., 16 (1980) 1009.

3 V.V. Litvak, P.P. Kun, V.D. Shteingarts, Zh. Org. Khim. 18 (1982) 1966.

4 V.V. Litvak, P.P. Kun, I.I. Oleynik, O.V. Volkov, V.D. Shteingarts, J. Organomet. Chem., 310 (1986) 189.

5 A.C. Knipe, S.J. McGuinness, W.E. Watts, J. Chem. Soc., Perkin Trans. II, (1981) 193.

6 T.B. Chenskaya, M.G. Ezernitskaya, B.V. Lokshin, Izv. Akad. Nauk SSSR, ser. khim., (1981) 459.

7 V.V. Litvak, P.P. Kun, V.D. Shteingarts, Zh. Org. Khim., 18 (1982) 2153.

8 J.F. Bunnett, H. Moe, D. Kuntson, J. Chem. Soc. 76 (1954) 3936.

9 S.M. Shein, L.A. Kozores, Reakts. sposobn. organ. soedin., 3 (1966) 45.

10 Yu.A. Zhdanov, V.I. Minkin, Correlation Analysis in Organic Chemistry, Izd. Rostovsk. gos. un-ta, 1966.

11 Spravochnik khimika, Khimia , 1964, Vol. 3, p. 959.

12 A.J. Gordon, R.A. Ford, The Chemists Companion, Moscow, Mir, 1976, p. 167, 172.

13 C.G. Swain, E.C. Laupton, J. Chem. Soc., 90 (1968) 4328.

14 N.B. Chapman, J. Shorter, Correlation Analysis in Chemistry. New York, London, Plenum Press, 1978, p. 455.

15 R.U. Taft M.S. Newman (Ed.), Steric Effects in Organic Chemistry, Moscow, Mir, 1960, p. 596.

16 P.R. Wells, Chem. Rev., 63 (1963) 171.

17 V.V. Litvak, L.S. Filatova, N.U. Halikova, V.D. Shteingarts, Zh. Org. Khim., 16 (1980) 336.

18 D.A. Brown, J.R. Rajn, J. Chem. Soc., A (1966) 40.

19 J.F. Bunnett, H. Herman, J. Org. Chem., 36 (1971) 4081.

20 V.V. Litvak, P.P. Kun, V.D. Shteingarts, Zh. Org. Khim. 20, (1984) 753.

21 V.V. Litvak, L.S. Filatova, V.D. Shteingarts, Zh. Org. Khim., 17 (1981) 1285.

22 P.P. Kun, V.V. Litvak, V.D. Shteingarts, Zh. Org. Khim., 20 (1984) 759.

23 B. Nichols, M.C. Whiting, J. Chem. Soc., (1959) 551.

24 F. van Meurs, A.J. Hoefnagel, B.M. Wepster, H. van Bekkum, J. Organomet. Chem., 142 (1977) 299.

25 E.I. Sirotkina, A.N. Nesmejanov, N.A. Vol'kenau, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1605.

26 A. Agarwal, M.J. McGlinchey, T.-S. Tan, J. Organomet. Chem., 141 (1977) 85.

27 H. Brunner, H. Koch, Chem. Ber., 115 (1982) 65.

28 D. Bethel, V. Gold, Carbonium Ions, Moscow, Mir, 1970.

29 N. Hao, M.J. McGlinchey, J. Organomet. Chem., 161 (1978) 381.

30 F. van Meurs, J.M.A. Baas, H. van Bekkum, J. Organomet. Chem., 113 (1976) 353.

31 E.W. Neuse, J. Organomet. Chem., 99 (1975) 287.

32 M. Herberhold, K. Leonhard, Chem. Ber., 107 (1974) 3222.

33 J. Müller, J. Organomet. Chem., 18 (1969) 321.

34 A.N. Nesmeyanov, I.F. Leshchova, Yu.A. Ustynyuk, Ye.T. Sirotkina, I.N. Bolesova, L.S. Isayeva, N.A. Vol'kenau, J. Organomet. Chem., 22 (1970) 689.

35 G.G. Dvoryanzeva, Yu.A. Sheinker, S.P. Gubin, Reacts. Sposobnost. Org. Soedin., 3 (1966) 86.

36 S.P. Gubin, K.I. Grandberg, E.G. Perevalova, A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 159 (1964) 1075.

37 W.F. Little, R. Eisenthal, J. Org. Chem., 26 (1961) 3609.

38 W.D. Kummler, J. Am. Chem. Soc., 60 (1938) 859.

39 J. C. Speakman, J. Chem. Soc., 855 (1940).

40 I.I. Oleynik, P.D. Kun, V.V. Litvak, V.D. Shteingarts, Zh. Org. Khim., 24 (1988) 929.