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SIDE-CHAIN REACTIONS IN π-CHROMIUM TRICARBONYL COMPLEXED ARENES

III*. STERIC AND ELECTRONIC EFFECTS ON THE EXCHANGE REACTION BETWEEN (BENZYL CHLORIDES)–CHROMIUM TRICARBONYL AND SODIUM THIOCYANATE IN ACETONE

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SUMMARY

The effects of substituents on the rates of bimolecular substitution of (benzyl chlorides)–chromium tricarbonyl with sodium thiocyanate in acetone are described. Except for the *p*-methoxy compound, all the complexes react more slowly than the corresponding uncomplexed benzyl chlorides. The decrease in reactivity on complexing is ascribed to the incursion of steric effects. While in the uncomplexed series there is a spectrum of transition states ranging from fully synchronous S_N2 to S_N1-like, complexation shifts the spectrum towards transition state structures with a well pronounced carbonium-like character. Thus, of the two opposing effects that the tricarbonyl chromium can produce at the α-reaction center, its electron-donating ability prevails over its electron-attracting effect.

INTRODUCTION

Although there has been increasing interest in the effect of the chromium tricarbonyl group on the reactivity of an arene ligand[1], the problem of the transmission of electronic effects from the chromium tricarbonyl and the reaction center is far from being solved[2]. If we restrict the investigation to side-chain reactions occurring at the α-carbon, it appears (depending on the electronic requirements of the reaction center at the transition state) that the rate is influenced differently by the presence of complexed arene. Thus, the ambivalent character of the $Cr(CO)_3$ group is well demonstrated in the so-called "limiting" substitution reactions, *i.e.* those in which the α-carbon has a well developed carbonium ion or carbanion character in the transition state. In the first case, in fact, complexation increases the rate by a factor of 10^3–10^5, depending on the structure of the carbonium ion itself[1a,d]. In the second case the rate also increases, though to a minor extent, on complexation[3]. The electron-

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* For Part II see ref. 3.

attracting power has been quantitatively compared to that of a *p*-nitro group[1b,c,★].

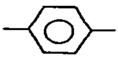
Due to the ability of the chromium tricarbonyl group to behave both as an electron-attracting and as an electron-donating substituent, it is of interest to see how complexation changes the reactivity in "borderline" substitution reactions[4]. In these reactions the gradual change of transition state structure, *i.e.* from S_N1 to S_N2, promoted by substituent, solvent, or the presence of salts in uncomplexed substrates, can, by complexation, be drastically shifted in one direction or the other according to which of the two contrasting effects prevails.

In the present study we describe kinetic results on the substitution reaction between complexed or uncomplexed benzyl chlorides and sodium thiocyanate in acetone. Some data are also given for the same reaction of 2-phenylethyl bromides.

RESULTS AND DISCUSSION

The rates of substitution of the benzyl chlorides, both complexed and un-

TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE EXCHANGE REACTION BETWEEN BENZYL CHLORIDES.XCH_2—Cl (COMPLEXED AND UNCOMPLEXED) AND SODIUM THIOCYANATE IN ANHYDROUS ACETONE

	X	*Temp.* (±0.1°C)	*k* × 10^4 [a] (*l*·*m*$^{-1}$·sec^{-1})	$\Delta H^{\neq}$ [b] (*kcal/mol*)	$\Delta S^{\neq}$ [b] (*e.u.*)
Uncomplexed series[c]	H	54.2	3.90		
		65.2	7.80	17.5	−21.0
		75.3	17.2		
		85.1	39.2		
	NO_2	45.0	6.90		
		55.0	16.0		
		65.0	35.0	16.4	−21.5
		75.0	79.1		
	Cl	65.0	13.2		
	Me	65.0	10.7		
	OMe	65.0	24.0		
Complexed series[d]	H	55.0	0.82		
		65.0	2.50	19.3	−18.5
		75.0	4.70		
		85.0	11.2		
	Cl	65.0	1.19		
	3-OMe	65.0	2.36		
	Me	65.0	6.32		
	OMe	65.0	28.6		

[a] Mean values from two different runs. Deviations were within the limits of experimental error. [b] At 65°. [c] Substrate: 0.1 *M*; sodium thiocyanate: 0.1 *M*. [d] Substrate: 0.02 *M*;

★ However, we have shown[3] that kinetic equivalence between the *p*-NO_2 and chromium tricarbonyl groups is not observed in the elimination from 2-phenylethyl bromide and *p*-toluene sulfonate to give styrene, where direct resonance between the electron-rich α-carbon and the substituent occurs.

TABLE 2

RELATIVE RATES OF EXCHANGE AT 65° BETWEEN SODIUM THIOCYANATE AND SUBSTITUTED BENZYL CHLORIDES OR 2-PHENYLETHYL BROMIDES.

Substrates	*Substituent*						
	4-NO_2	*4-Cl*	*3-OMe*	*4-H*	*4-Me*	*4-OMe*	
Benzyl chlorides (uncomplexed)	4.50	1.70		1.00	1.40	3.10	
Benzyl chlorides (complexed)		0.50	0.95	1.00	2.50	11.5	
k (complexed)/ *k* (uncomplexed)		0.09		0.30	0.60	1.20	
2-Phenylethyl bromides	2.70	1.50		1.00		0.80	2.30[a]

[a] $Cr(CO)_3$.

complexed, together with some of the activation parameters are listed in Table 1. Relative rates at 65° for both series of compounds (Table 2) indicate the extent to which the rate is influenced by substituents in the aryl ring. Application of the Hammett equation to the uncomplexed chlorides (Fig. 1, dashed line) gives the usual U-shaped curve, where both electron-donating and electron-attracting groups are activating relative to hydrogen. Similar curves have been found in substitution reactions of benzyl derivatives, both in hydroxylic[5,6] and in aprotic solvents[6]. This borderline behaviour is rationalized by the fact that the structure of the substrate is so modified by substituents that the relative importance of bond making and breaking at the transition state is continuously changing, so that the reaction con-

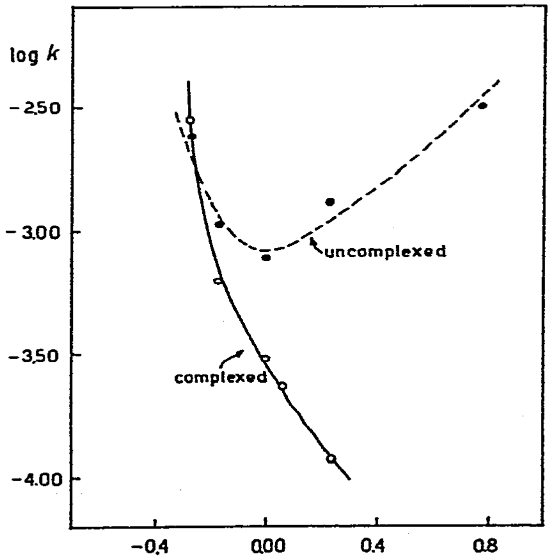
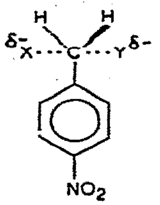
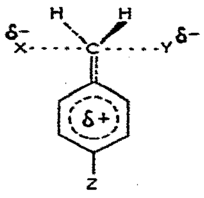


Fig. 1. Hammett plot for exchange reaction between benzyl chlorides (complexed, solid line; uncomplexed, dashed line) and sodium thiocyanate in acetone at 65°.

stant ρ of the Hammett equation also changes continuously. This behaviour has recently been excellently discussed by Parker and his co-workers[6], who described the extreme structures of the spectrum as "tight" and "loose" transition states. The "tight" structures, (I), corresponding to a fully synchronous S_N2 process, are favoured by electron-attracting groups, as *p*-nitro. The "loose" transition state, (II), which corresponds to a bimolecular process still having S_N1 character, is preferred when electron-donating substituents, Z, are attached to the ring.



(I)

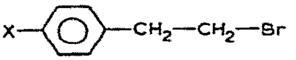


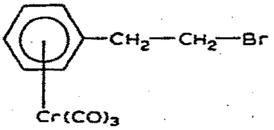
(II)

A priori one would expect that the tricarbonyl moiety would be capable of stabilizing both structure (II), by its extraordinary ability to delocalize a positive charge at the α-carbon[1a,d], and structure (I), by its strong electron-attracting effect[1d,3].

We first consider the effects of substituents and of complexing for the same reaction involving 2-phenylethyl bromides (Tables 2 and 3). In this case, the uncomplexed substrates do not display a "borderline" behaviour, and the Hammett corre-

TABLE 3

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE EXCHANGE REACTION BETWEEN 2-PHENYLETHYLBROMIDES,  AND SODIUM THIOCYANATE IN ANHYDROUS ACETONE[a]

X	*Temp.* (±0.1°C)	$k \times 10^4$[b] ($l \cdot m^{-1} \cdot sec^{-1}$)	$\Delta H^{\neq}$[c] (*kcal/mol*)	$\Delta S^{\neq}$[c] (*e.u.*)
H	55.0	6.90		
	65.3	15.6	16.2	−23.5
	75.1	30.0		
	85.4	64.0		
NO_2	45.0	7.70		
	54.2	16.8		
	65.2	36.6	16.6	−20.5
	75.2	83.4		
Cl	75.0	45.0		
OMe	75.0	23.5		
	45.0	7.10		
	55.0	15.2		
	65.1	31.0	16.2	−22.0
	75.0	70.5		

[a] Substrate: 0.02 *M*; sodium thiocyanate: 0.1 *M*, [b] Mean values of two different runs. Deviations were within the limits of experimental error. [c] At 65°.

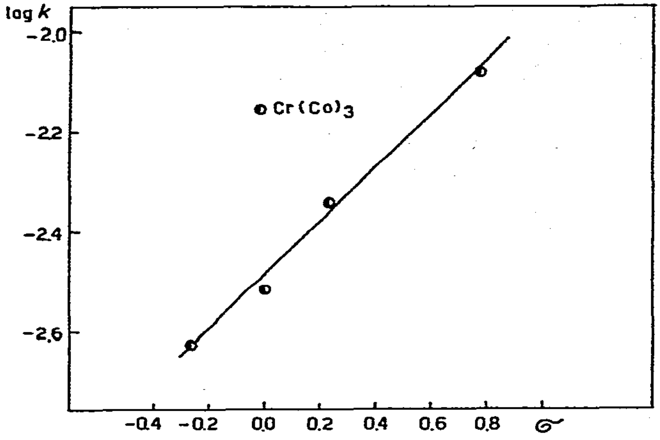


Fig. 2. Hammett plot for exchange reaction between 2-phenylethyl bromides and sodium thiocyanate in acetone at 75°.

lation is linear (Fig. 2) with a ρ value, $+0.56 \pm 0.04$*, (correlation coefficient $r=0.994$). It is likely that a fully synchronous S_N2 process is operating for all members of the series, and so only electron-attracting substituents accelerate the reaction. The parent complexed bromide reacts faster than the uncomplexed analog ($k_{\mathrm{Cr(CO)_3}}/k_{\mathrm{H}}=2.3$), and the accelerating effect of Cr(CO)$_3$, due to its electron-attracting power, is only slightly lower than that of a *p*-nitro group ($k_{p\text{-}\mathrm{NO_2}}/k_{p\text{-}\mathrm{H}}=2.7$).

We return now to the benzyl systems. As one moves along the dashed curve of Fig. 1 from electron-donating to electron-attracting substituents, the "loose" transition state (II) becomes less and less important. Therefore the chromium tricarbonyl should participate less in stabilization of a carbonium like species; however the electron-attracting effect, which favours the formation of "tight" transition state (I), should still be present. In any case, the reactivity of complexed chlorides is expected to be higher than that of uncomplexed chlorides. In fact, all the complexed chlorides, except *p*-methoxy chloride, react more slowly than the uncomplexed analogs (Fig. 1, solid line). The *p*-chloro for example, is eleven times less reactive than the uncomplexed chloride; however the $k_{\mathrm{complexed}}/k_{\mathrm{uncomplexed}}$ ratio increases steadily as one moves towards more electron-donating substituents, and it becomes greater than unity for *p*-methoxy (Table 2, third line).

As far as we are aware, this is the first case in which the complexing of an arene with Cr(CO)$_3$ decreases the reactivity at the α-carbon of the side-chain. It is quite certain that the decreased rate cannot be attributed to electronic influences, in view of the characteristic "borderline" nature of the substituent effects, which requires that any substituent is activating relative to hydrogen. The effect therefore must be steric; it is likely that steric hindrance to the approaching nucleophile SCN$^-$ at the benzylic carbon is much more pronounced when the ligand is complexed, and the bulky chromium tricarbonyl interferes with the entering and leaving groups in the transition state. In the 2-phenylethyl series, in which the attack of the nucleophile

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* This value is very close to that obtained for the substitution of 2-phenylethyl chlorides by iodide ions in acetone, $\rho=+0.53$[7].

occurs at the more remote β-carbon, the $Cr(CO)_3$ does not interfere sterically with the entering thiocyanate or the leaving bromide ion, the rate increases on complexing, and this is mostly ascribed to the strong electron-attracting power of the chromium tricarbonyl.

However, the extent of the steric effect in the benzylic series is difficult to evaluate. For "tight" transition state (I) steric interactions should be of prime importance, but they should become less and less significant as the "loose" transition state (II) becomes more favoured. It is of importance, therefore, to know which type of transition state structure the complexed compounds utilize. The shape of the Hammett correlation is revealing in this connection. Unlike the uncomplexed substrates, the complexed chlorides do not exhibit a U-shaped curve, the effect of substituents being monotonic (though not linear), the rate decreasing from electron-donating to electron-attracting groups (Fig. 1). The lack of a right arm of the curve corresponding to a positive ρ value indicates that for all the compounds examined the transition state has a carbonium like character, *i.e.* the importance of bond breaking prevails over that of bond making. Thus, between the two contrasting effects that the chromium tricarbonyl can produce, the electron-donating ability prevails over its electron-attracting effect. However, it is striking that, even though "loose" transition states are preferred by the complexed derivatives, the steric factors introduced by the bulky $Cr(CO)_3$ still predominate over electronic effects, so that in most cases the complexing results in a lowered reactivity.

The presence of a blend of steric and electronic effects in the complexed series is clearly reflected in the different slopes of the left arm of the two curves of Fig. 1. The slope of the solid line is steeper than that of the dashed one; in other words the Hammett constant ρ is more negative for the complexed series. In those reactions for which the substituent effects have been examined[1b,2], the opposite trend is usually found, *i.e.* the value of ρ is always lower (less positive) in the complexed than in the uncomplexed series. This has been attributed to the fact that electronic changes at the reaction center are less important in the complexed compounds, the effective charge, both positive and negative, being greatly diminished by the metal in the parent compound. Further substitution in the aryl ring will thus influence the situation less than it would in the uncomplexed system. If, as in our case, the introduction of a substituent has a greater effect in the complexed than in the uncomplexed series, this is because an electron-donating substituent shifts the transition state towards a "looser" carbonium like structure, and in doing so removes some of the steric interactions. Consequently the difference of the rate constants between two correspondingly substituted compounds (one uncomplexed and the other complexed) decreases as one moves to the left of the curve, *i.e.* as the substituent becomes more electron-donating, up to the point at which the two curves cross; the reactivities then invert, and so the complexed *p*-methoxy compound reacts faster than the uncomplexed analog.

We are extending our studies to other types of reactions in an effort to elucidate further the electronic and steric effects of the chromium tricarbonyl group.

EXPERIMENTAL

Melting points are uncorrected. The microanalyses were by Dr. E. Celon, Istituto di Chimica Organica, Padova (Italy).

Solvents and materials

Commercial Reagent Grade acetone was refluxed over potassium permanganate and distilled. From redistillation over potassium carbonate the fraction b.p. 56.4–56.5° was collected. Commercial Reagent Grade sodium thiocyanate was dried and stored over P_2O_5. 4-Substituted benzyl chlorides and 2-phenylethyl bromide were redistilled or recrystallized products of Reagent Grade.

2-(*p-Nitrophenyl*)*ethyl bromide*

2-(*p*-Nitrophenyl)ethyl bromide was obtained by nitration of 2-phenylethyl bromide, as described by Foreman[8]. M.p. 69° (lit.[8] 69–70°).

2-(*p-Anisyl*)*ethyl bromide and* 2-(*p-chlorophenyl*)*ethyl bromide*

These were prepared from the corresponding alcohols[9] by treatment with phosphorus tribromide.

2-(*p*-Anisyl)ethyl bromide: B.p. 68–69°/0.01 mmHg. (Found: C, 5.10; H, 5.05; Br, 37.1. $C_9H_{11}BrO$ calcd.: C, 5.02; H, 5.15; Br, 37.1%)

2-(*p*-Chlorophenyl)ethyl bromide: b.p. 69–70°/0.05 mmHg. (Found: C, 43.7; H, 3.60; Br, 36.45; Cl, 16.05. C_8H_8BrCl calcd.: C, 43.75; H, 3.65; Br, 36.40; Cl, 16.15%.)

(*2-Phenylethyl bromide*)*chromium tricarbonyl*

This compound was obtained as in ref. 3.

(*Benzyl alcohols*)*–chromium tricarbonyl*

The (*p*-CH_3, *m*-OCH_3 and *p*-Cl-benzyl alcohols)–chromium tricarbonyl complexes were prepared by reduction with $LiAlH_4$ in ether of the appropriate (benzoic methyl ester)—chromium tricarbonyl complexes which in turn were obtained by direct complexation of hexacarbonylchromium with aromatic esters as described by Klopman[1b]. The (*p*-H and *p*-OCH_3-benzyl alcohols)–chromium tricarbonyl were prepared from hexachromium tricarbonyl and benzyl alcohols and *p*-methoxybenzyl alcohols. The complexes were purified by recrystallization from ether/light petroleum or benzene/light petroleum. NMR and IR spectra were as expected.

The following melting points and elemental analyses were obtained:

Parent, m.p. 95° (lit.[1a] 94–95°). (Found: C, 49.0; H, 3.20. $C_{10}H_8Cr$ calcd.: C, 49.2; H, 3.30%.)

p-Methoxy, m.p. 62–64° (lit.[2a] 60–62°). (Found: C, 49.4; H, 3.80. $C_{11}C_{10}CrO_5$ calcd.: C, 48.2; H, 3.65%.)

m-Methoxy, m.p. 106–107° (lit.[11] 106°). (Found: C, 48.7; H, 3.60. $C_{11}H_{10}CrO_5$ calcd.: C, 48.2; H, 3.65%.)

p-Chloro, m.p. 89° (lit.[2a] 88–89°). (Found: C, 44.2; H, 2.50; $C_{10}H_7ClCrO_4$ calcd.: C, 43.1; H, 2.55%.)

(*Benzyl chloride*)*chromium tricarbonyl complexes*

(Benzyl alcohol)–chromium tricarbonyl complexes were converted into the corresponding chlorides by shaking the benzene solutions with HCl, except that the *p*-methoxybenzyl chloride was obtained by bubbling anhydrous HCl into a cooled ether solution of the complexed alcohol. Recrystallization from light petroleum gave the chlorides. IR and NMR spectra were consistent with their structure. Acceptable volumetric analyses of the chloride ion were obtained for all compounds. Melting points: parent, 63–64° (lit.[1a] 63–64°); *p*-methoxy, 59–60°; *p*-methyl, 99.5–100°; *m*-methoxy, 56°; *p*-chloro, 99°.

(Benzyl thiocyanate)chromium tricarbonyl

The compound has been described previously[1d].

Kinetic measurements

Solution of the organic chloride (or bromide) and sodium thiocyanate were mixed at room temperature to give the desired concentrations of reactants. 5 ml portions of the solution were transferred to ampoules and a stream of pre-saturated nitrogen was bubbled through. Then they were sealed and put in thermostat; at appropriate time intervals the ampoules were withdrawn, the solution and the precipitated NaCl poured into ether, and the organic layer extracted three times with cold water. The aqueous extracts were treated with H_2O_2 and H_2SO_4 (or KOH) and boiled for 10 min. The residual H_2O_2 was destroyed by boiling the solution in the presence of a platinum wire. After cooling the chloride ion was determined by the Volhard method.

Good plots of the second-order rate law were obtained up to 80% conversion, and the reproducibility of the rate constants was good. The infinity titres were always more than 96% of the theoretical. No appreciable decomposition was observed in the complexed substrates even at the highest concentration, *viz.* 0.1 *M*. At least six points were determined in each run, and the rate constants given in the Tables are averaged values taken from a minimum of two independent runs.

Product analysis

The reaction between the parent uncomplexed benzyl chloride and sodium thiocyanate in acetone gave benzyl thiocyanate in a more than 90% yield. The IR spectrum of the product did not show any band characteristic of isothiocyanate (2085 cm^{-1}). In contrast, when complexed benzyl chloride (1.1×10^{-2} mol) was treated with excess NaSCN (1 mol) in acetone (overnight at room temperature), the crude product contained some isothiocyanate (ca. 5%). Recrystallization from ether/petroleum ether gave pure complexed thiocyanate in a 90% yield. The presence of the isothio isomer is due to the high rate of isomerization of complexed thiocyanate, which is $>10^4$ times greater than that of the uncomplexed substrate[1d]. Under kinetic conditions it was observed that when the displacement reaction was taken only to 50%, no isothio isomer was present, but after 4 half-lives the ratio thio/isothio was 3.6/1. The amount of isothio isomers present at various times can be satisfactorily accounted for in terms of the known first-order rate coefficient for the isomerization.

In the reaction between 2-phenylethyl bromide and sodium thiocyanate, IR analysis of the crude product showed only the band of the *thio* isomer, both in uncomplexed and complexed substrates. *A priori* for the same compounds, the thiocyanate ion might bring about elimination of hydrogen bromide to give styrene, in addition to the substitution reaction, but no (< 0.1%) olefin could be detected after 10 half-lives. Blank experiments showed that the possible olefins would be stable under the reaction conditions.

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