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CORRELATIONS OF SUBSTITUENT PARAMETERS WITH THE CARBONYL STRETCHING FORCE CONSTANT IN ARENETRICARBONYLCHROMIUM COMPLEXES

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Summary

Correlations are established between selected substituent parameters (σ_I, σ_P, $\sigma_R{}^P$, $\sigma_P{}^o$, $\sigma_R{}^o$) and the carbonyl stretching force constant, k(CO), for 28 mono- and poly-substituted tricarbonylchromium-complexed arene compounds. On the basis of the statistical results it is concluded that the overall electronic substituent effect transmitted to the carbonyl groups involves both mesomeric and inductive mechanisms. Within the restricted domain, including substituent group and benzene ring, transmission proceeds largely by resonance, with a minor inductive (through-bond and field) effect operative in the same domain. Further transmission from the substituted arene ring to the chromium atom predominantly involves an inductive mechanism. This result, in support of existing literature data, suggests appreciable participation of the ring carbon σ framework in the metal—ring bond formation.

Introduction

The first attempt to correlate electronic substituent effects with carbonyl stretching frequencies, ν(CO), in arenetricarbonylchromium complexes was reported by Fischer [1], who recognized the existence of a qualitative relationship between ν(CO) and Hammett σ values for a large number of tricarbonylchromium-complexed benzene derivatives. Other authors [2-5] subsequently derived more quantitative linear correlations between k(CO), the CO stretching force constant, and σ_P values for selected complexes. The usefulness of k(CO) as a measure of the changes in electron density brought about on the metal nucleus by a substituent on the benzene ring was thus established. It was concluded [2, 6,15] that a large variation of charge can be accommodated by the tricarbonylchromium function through a mechanism of withdrawal from, and back-donation into, the ring, thereby "buffering" electronic interaction from one substituent to another on the aromatic ring.

In connection with studies of oligomeric and polymeric chromium-complexed arenes we wished to gain a clearer understanding of the mode by which electronic substituent effects are transmitted across the metal atom. For this reason, we established and compared the degrees of correlation attainable in the linear relationships between k(CO), on the one hand, and selected Hammett and Taft substituent constants, on the other hand, for 28 mono- and poly-substituted tricarbonylchromium-complexed benzene derivatives. The results are reported below.

Results and discussion

The complexes selected, prepared from the respective benzene derivatives and chromium hexacarbonyl by modified literature procedures [7-16], are listed in Table 1. They include 14 monosubstituted (I-XIV) and 13 *ortho-*, *meta-* and *para*-disubstituted complexes (XV-XXVI) in addition to 1,3,5-trimethyl- (XXVII) and hexamethyl-benzene (XXVIII). Seven of the disubstituted complexes (XV-XIX, XXIV, XXVI) possess substituent groups of the identical type, whereas four (XX-XXIII) are characterized each by having a $+M$ and a $-M$ substituent in *o-* or *p*-position so as to exhibit through-resonance. The table also presents the observed IR frequencies of the totally symmetric A_1 and the two degenerate E carbonyl stretching vibrations and the carbonyl stretching force constants k(CO) calculated by use of the Cotton—Kraihanzel approximation [17].

The following substituent constants were chosen for comparison in this study: σ_I, σ_P, σ_R^P, σ_P^o, and σ_R^o. Hammett's constant, σ_P, is a measure of the total inductive and mesomeric electronic effect exerted by a substituent group onto the detection center (here: the carbonyl groups). The inductive component, representing the combination of a diminishing-relay effect through the compound's σ framework and a polar field effect operating through space, is measured by Taft's σ_I, whereas σ_R^P describes the corresponding (unexalted) resonance component implying electronic delocalization from or to the substituent group as "seen" by the detection center. Taft's polar resonance constant σ_R^o specifically measures the resonance effect operative in the restricted domain between substituent and benzene ring, while the normal Taft parameter σ_P^o reflects the purely inductive effect exerted by the (*para*-substituted) arene ring's carbon σ and π framework onto the detection center [18,19]. The values, taken from the literature [22-29], are listed in the subsequent columns of Table 1; the entries for the polysubstituted complexes are composite parameters obtained by summation of the respective constants for each substituent group. The additivity of substituent constants in correlation experiments has been demonstrated in the literature [2,3,5,30]; in the present case, justification for use of this approach was derived from preliminary correlation studies, which showed no significant changes when some or all of the listed polysubstituted compounds were omitted from the investigation either individually or in groups (e.g., all *m-* or *p*-disubstituted compounds, all *p*-through-conjugated compounds, etc.).

Table 2 summarizes the statistical information derived from correlations of k(CO) with each type of σ parameter taken from Table 1. The data, obtained by a least-squares fitting, include slope and intercept for the regression line $k(\text{CO}) = b_0 + b_1\sigma$, estimate of standard derivation s, and correlation coefficient r.

TABLE 1

CO STRETCHING FREQUENCIES, FORCE CONSTANTS, AND SELECTED σ PARAMETERS OF SUBSTITUTED BENZENETICARBONYLCHROMIUM COMPLEXES

Complex No.	Arene ligand	Lit.	ν(CO)[a] (cm^{-1})		k(CO) (10^5 dyn cm^{-1})	Substituent parameters[b]				
			A_1	E		σ_I[c]	σ_p[d]	σ_R^p[e]	σ_p^o[f]	σ_R^o[g]
I	Benzene	7	1975	1893	14.898	0	0	0	0	0
II	Toluene	7[h]	1970	1887	14.810	−0.05	−0.17	−0.11	−0.12	−0.10
III	Ethylbenzene	13[h]	1970	1888	14.820	−0.05	−0.15	−0.10	−0.12	−0.10
IV	Isopropylbenzene	13	1964	1884	14.748	−0.04	−0.15	−0.11	−0.15	−0.12
V	Biphenyl	8	1968	1890	14.830	0.10	−0.01	−0.11	0.05	−0.10
VI	Anisole	7	1965	1882	14.733	0.26	−0.26	−0.52	−0.10	−0.41
VII	Ethoxybenzene	[j]	1965	1882	14.733	0.26	−0.24	−0.50	−0.12	−0.44
VIII	Diphenyl ether	[j]	1967	1886	14.784	0.38	−0.32	−0.70	0.08	−0.36
IX	Aniline	7	1961	1872	14.611	0.10	−0.66	−0.76	−0.36	−0.48
X	*N,N*-dimethylaniline	7,9	1952	1864	14.483	0.05	−0.83	−0.88	−0.48	−0.52
XI	Acetophenone	7	1980	1908	15.078	0.28	0.43	0.15	0.49	0.19
XII	Methyl benzoate	7	1981	1908	15.083	0.31	0.45	0.14	0.46	0.15
XIII	Bromobenzene	12	1976	1900	14.975	0.45	0.23	−0.22	0.31	−0.16
XIV	Chlorobenzene	7,9	1977	1898	14.960	0.47	0.23	−0.24	0.29	−0.20
XV	*p*-Dimethoxybenzene	11	1962	1878	14.677	0.52	−0.52	−1.04	−0.20	−0.82
XVI	*p*-Diethoxybenzene	[j]	1961	1877	14.661	0.52	−0.48	−1.00	−0.24	−0.88
XVII	*p*-Phenylenediamine	16	1953	1862	14.468	0.20	−1.32	−1.52	−0.72	−0.96
XVIII	Terephthalaldehyde	[j]	1989	1929	15.343	0.62	0.44	−0.18	1.06	0.52
XIX	Dimethyl terephthalate	10	1999	1928	15.386	0.62	0.90	0.28	0.92	0.30
XX	*p*-Fluorotoluene	7,15	1973	1893	14.887	0.46	−0.09	−0.54	0.10	−0.44
XXI	*p*-Aminoacetophenone	4[i]	1969	1890	14.836	0.38	−0.23	−0.61	0.13	−0.29
XXII	*p*-Toluidine	7,15	1955	1868	14.539	0.05	−0.83	−0.87	−0.48	−0.58
XXIII	*o*-Toluidine	7	1954	1867	14.524	0.05	−0.83	−0.87	−0.48	−0.58
XXIV	*o*-Dimethoxybenzene	11	1960	1876	14.646	0.52	−0.52	−1.04	−0.20	−0.82
XXV	*m*-Chloroaniline	4	1966	1886	14.779	0.57	−0.43	−1.00	−0.07	−0.68
XXVI	*m*-Dimethoxybenzene	11	1961	1876	14.651	0.52	−0.52	−1.04	−0.20	−0.82
XXVII	1,3,5-Trimethylbenzene	7	1957	1876	14.620	−0.15	−0.51	−0.33	−0.36	−0.30
XXVIII	Hexamethylbenzene	7	1949	1861	14.432	−0.30	−1.02	−0.66	−0.72	−0.60

[a] In dichloromethane solution. [b] $\Sigma\sigma$ for complexes XV-XXVIII. [c] From refs. 19,23 (complex XVIII from ref. 23). [d] From refs. 21,22 (complex XVIII from ref. 20). [e] From preceding two columns ($\sigma_R^p = \sigma_p - \sigma_I$). [f] From refs. 27-29. [g] From refs. 19,26 (complex XVIII from ref. 25). [h] Sample supplied by Dr. C. Segard. [i] Sample supplied by Dr. P.C. Reeves. [j] This work.

TABLE 2

k(CO)—σ CORRELATIONS[a]

Substituent parameter	b_1 (10^5 dyn cm^{-1})	b_0 (10^5 dyn cm^{-1})	s (10^5 dyn cm^{-1})	r
σ_I	0.469	14.667	0.204	0.510
σ_p	0.456	14.906	0.069	0.957
σ_R^p	0.391	14.986	0.157	0.748
σ_p^o	0.551	14.810	0.042[b]	0.984[b]
σ_R^o	0.529	14.967	0.129[c]	0.839[c]

[a] For regression line $k(CO) = b_0 + b_1\sigma$; $n = 28$. [b] For σ_p^n: $s = 0.058 \times 10^5$ dyn cm^{-1}, $r = 0.970$. [c] For σ_R^n: $s = 0.160 \times 10^5$ dyn cm^{-1}, $r = 0.738$.

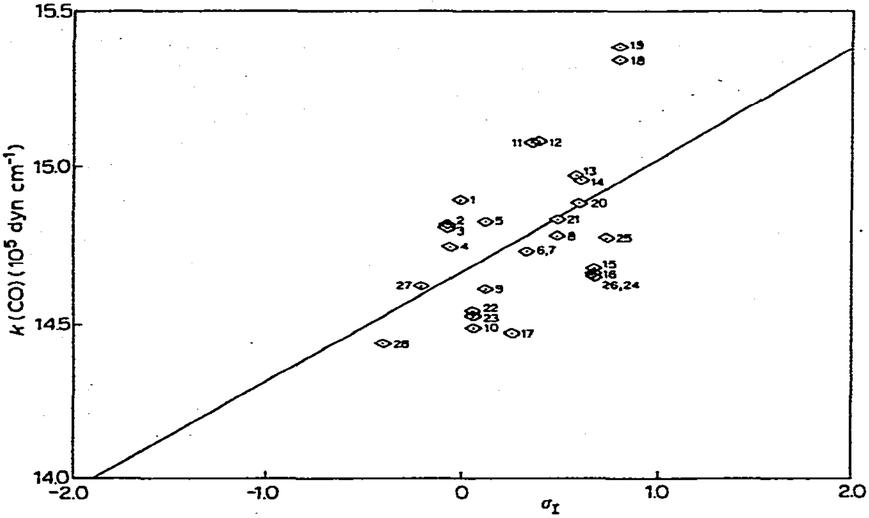

Fig. 1. k(CO)—σ_I correlation; $r = 0.51$; $s = 0.20 \times 10^5$ dyn cm^{-1}.

The tabulated results permit the following interpretations:

(i). The poor correlation with σ_I ($r = 0.51$; $s = 0.20 \times 10^5$ dyn cm^{-1}; Fig. 1) shows that there is very little inductive transmission of the electronic effect from the substituent to the detection center either through the arene ring's σ framework or directly through space. This is, of course, what one would expect in view of the appreciable spatial separation of the carbonyl groups from the substituents.

(ii). A very much better correlation is apparent for σ_P ($r = 0.96$; $s = 0.07 \times 10^5$ dyn cm^{-1}), indicating that a mesomeric mechanism plays a significant, although at this point unsatisfactorily defined role in the conveyance of the elec-

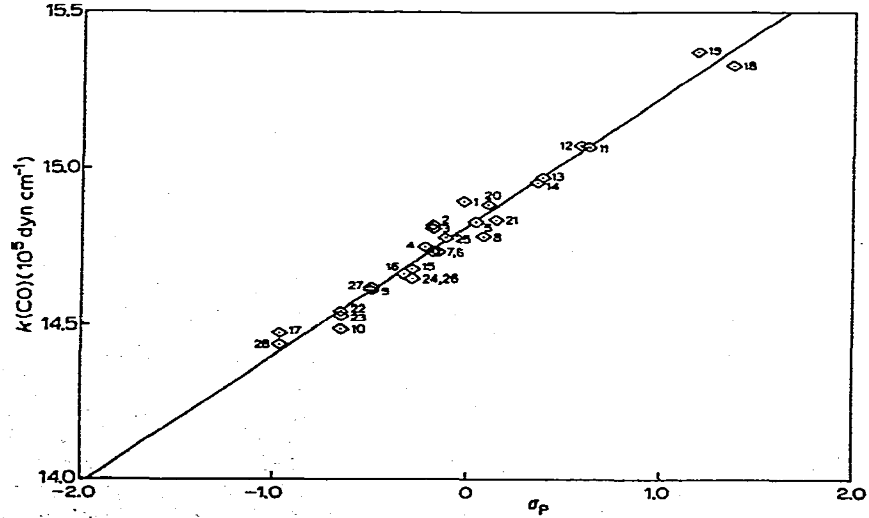

Fig. 2. k(CO)—$\sigma_P{}^0$ correlation; $r = 0.98$; $s = 0.04 \times 10^5$ dyn cm^{-1}.

tronic substituent effects in these complexes. Resonance is not, however, the exclusive mechanism of transmission, as is seen from the considerably poorer correlation established for σ_R^P ($r = 0.75$; $s = 0.16 \times 10^5$ dyn cm^{-1}).

(iii). The restriction implicit in the foregoing conclusion finds support in the correlations derived for Taft's constants. The polar resonance parameter σ_R° shows a better correlation ($r = 0.84$; $s = 0.13 \times 10^5$ dyn cm^{-1}) than does σ_R^P; this suggests that, within the limited domain comprising substituent and benzene ring, the overall substituent effect transmitted to the carbonyl groups operates largely through a resonance mechanism, although the correlation is sufficiently imperfect to allow a minor contribution of an inductive mechanism within the same domain. Information about the mode of further transmission from the ring system to the carbonyl ligands can now be gained from the correlation coefficient associated with σ_P°. The excellent correlation observed ($r = 0.98$; $s = 0.04 \times 10^5$ dyn cm^{-1}; Fig. 2), well exceeding that of any other σ parameter investigated*, clearly shows the transmission mechanism within this domain to be almost entirely inductive in nature. It is thus evident that some region within the arene—chromium—carbonyl bond system lacks a suitable mechanism for significant electronic delocalization through π overlap. The Cr—CO bonds possess considerable π character resulting from resonance back-donation from chromium $3d$ to carbonyl π^* orbitals [17,31-34,38] and so do not qualify as efficient insulating systems that could prevent resonance with the detection center**. Therefore, the region impeding electronic delocalization can reasonably be expected to be found in the bond system connecting the metal with the arene ring. We conclude that the net electronic charge transfer from ligand to metal in the process of coordination involves not so much the ligand's π electron system, as had earlier been assumed [2,35,36], but rather affects electronic charge of the σ framework of the ring. This implies that the metal—ring bond possesses appreciably more σ character than can be attributed to the a_1-symmetry interactions of the ring's π cloud alone. With chromium $4s$ and $4p$ orbital populations in the ground state considered negligible [34], this bonding contribution from the ring carbon σ framework for the most part presumably involves interaction of metal d_{z^2} with arene carbon $2s$ and $2p_\sigma$ orbitals***.

The assumption of appreciable involvement of the ring's σ framework in metal—ring bond formation finds support in the insensitivity of the arene ring's π-electron system to (and the lack of significant change of π-electron density upon) complexation, which is apparent from theoretical treatments [37,38] and is reflected in the commonly observed invariance (relative to the free ligand) of NMR shifts of uncoordinated-ring protons in mono-complexes of conjugated

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* Wepster's [29] closely related parameters σ_P^n and σ_R^n, evaluated in this study for comparison, give poorer correlations with k(CO) (Table 2) than do Taft's parameters. There is no apparent benefit in their inclusion in the present discussion.

** A Mulliken—Wolfsberg—Helmholz SCF treatment of benzenetricarbonylchromium by Carroll and McGlynn [34] indicates π back-donation to CO (0.64 e$^-$) to exceed forward σ donation to Cr (0.53 e$^-$); confirming this trend, Brown and Rawlinson's SCC calculation [38] gives a π overlap population (0.329) nearly twice as large as the σ overlap population (0.169) for the Cr—CO bond.

*** Interactions of this type are clearly feasible on overlap grounds: SCF orbital overlap calculations [34] suggest the involved $3d_\sigma$—$2s$ and $3d_\sigma$—$2p_\sigma$ overlap integrals in benzenetricarbonylchromium to amount to 0.255.

[39-43] or fused [44] dinuclear aromatics* and other experimental results recently reported [4,11,42,45-47]. Further evidence supporting the importance of the σ framework in metal—ring bonding was derived by Gubin's group [42, 48]; from polarographic and ^{19}F NMR data, these authors inferred an appreciable increase, upon coordination, in ring-carbon electronegativity (i.e. effective positive charge), amounting to about 0.4 Pauling units, and concluded that "coordination with metal concerns σ rather than π orbitals" of the ring [48]. The bonding situation may thus be compared with the one in ferrocene, for which recent MO calculations [49], contrasting with earlier publications, suggest the participation of the ring carbon σ framework in metal—ring bonding to be at least as important as that of the ring's π electron system.

It is of interest to recall that ring-to-ring resonance interaction, i.e. electronic delocalization across the metal center, is not significant in the ferrocene nucleus [49,52]. This observation accords with major σ-framework participation as suggested [49]; in addition, it leads to the conclusion that the existing ring π-electron contribution, mostly involving e_1 orbitals [53-55], is insufficient to allow appreciable interannular delocalization. The parallel with benzenetricarbonylchromium is obvious, and very similar arguments may hold for complexes of this type. Differing from the situation in ferrocene, however, in which δ back-donation from filled Fe d_{xy,x^2-y^2} orbitals to the empty ring e_{2g} orbitals is not substantial [53,54,56,57], an appreciable extent of such δ back-bonding, involving the corresponding Cr d_{xy,x^2-y^2} and ring e_2 orbitals, is generally accepted [2,6,31,58-60] in the arenechromium complexes. In order to assess the effect of such back-bonding on electronic delocalization across the chromium atom, we determined the $k(\text{CO})$—σ_P° correlation for a selected group A of complexes comprising those from Table 1 that possess solely electron-accepting substituents. On the premise that increased back-donation to the ring, as caused by the enhanced electron demand of the substituent, would increase resonance between metal and ring in accordance with Brown's simple resonance model [31, 41,61], one should expect the $k(\text{CO})$—σ_P° correlation to be distinctly poorer (lower r, higher s) in the case of group A than in the case of the entire set of

TABLE 3

$k(\text{CO})$—σ_P° CORRELATIONS FOR SELECTED COMPLEXES WITH EITHER WITHDRAWING (GROUP A) OR DONATING (GROUP B) SUBSTITUENTS

Sample group	s (10^5 dyn cm^{-1})	r
A (withdrawing)[a]	0.040	0.976
B (donating)[b]	0.048	0.942
All 28 compounds[c]	0.042	0.984

[a] Group comprising all complexes with electron-donor substituents taken from Table 1 (XI-XIV, XVIII, XIX). [b] Group comprising complexes with electron-attracting substituents randomly selected from Table 1 (II, IV, X, XV, XVII, XXII). [c] Values taken from Table 2.

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* Contrasting with the behavior of tricarbonylchromium complexes, a considerable degree of bond fixation and concomitant loss of aromaticity has been observed [50,51] in the coordinated ring of tricarbonyliron compounds.

complexes investigated or, for that matter, of a control group B composed of complexes possessing solely electron-donating substituents. The statistical data derived are given in Table 3.

Although the correlations compared must be regarded with reservation because of the restricted sample size and the lack of randomness of selection in group A, there is clearly no trend in the direction of poorer k(CO)—$\sigma_P°$ correlation for the selected complexes with electron-attracting substituent groups. This would seem to indicate that chromium—ring δ back-donation is less pronounced than heretofore accepted. One cannot, however, dismiss the alternative conclusion that the decreased metal—carbonyl π back-donation accompanying the enhanced back-bonding to the ring in the A-group complexes merely entails a shift of multiple-bond character from the Cr—CO to the Cr—ring bond, while keeping the overall "insulating" effect within the ring—metal—carbonyl bond system, and, hence, the k(CO)—$\sigma_P°$ correlation, substantially unchanged. An extension of Brown's orbital population analysis [38] to the Cr—ring and Cr—CO π overlap in representative complexes of group A might shed more light on this question.

Experimental

Tricarbonylchromium complexes

The complexes listed in Table 1 were prepared from the respective arenes and chromium hexacarbonyl by the standard procedure of Nicholls and Whiting [7], modified by Strohmeyer [62] and other authors [8-16], except that di-n-butyl ether was used in place of higher-boiling solvents (in conjunction with commensurately extended heating times) in those reactions that produced complexes of limited thermal stability possessing electron-withdrawing substituent groups. Complexes VII, VIII and XVI, prepared in di-n-butyl ether (15-20 h), form yellow crystals melting at 72-73°, 87.5-88°, and 105-106°C, respectively. The dialdehyde complex XVIII, m.p. 107-108°C, was prepared by complexation of terephthalaldehyde tetra(ethyl acetal) [63] (28 h in refluxing di-n-butyl ether) and subsequent hydrolysis by the method described [15] for the synthesis of the *p*-tolualdehyde complex. All products were purified by passage through a short silica gel column in hexane or hexane/ether solutions and recrystallization from heptane or hexane/benzene. The solvents used for complexation and work-up were dried over Molecular Sieves, type 4A, and were thoroughly deoxygenated. Complexes II, III and XXI were obtained from Drs. C. Segard [14] and P.C. Reeves [4].

Infrared spectra and k(CO)—σ correlations

The IR spectra within the region of interest (1700-2000 cm^{-1}) were recorded on dichloromethane solutions with the use of a Perkin—Elmer, Model 521, spectrometer equipped with grating optics. A doubly expanded scanning scale was employed, and the spectra were calibrated by means of a polystyrene spectrum. The A_1 and E ν(CO) frequencies taken from the spectra and reported in Table 1 are accurate to ±1 cm^{-1}. Stretching force constants, k(CO), were calculated from the A_1 and E frequencies by the Cotton—Kraihanzel approximation [17]. The k(CO)—σ correlations were established with the use of a BESFIT program adapted to a Hewlett—Packard 9862A Calculator Plotter.

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